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En Route to Chiral-at-Metal Ruthenium Complexes Containing Tripodal Tetradentate Ligands

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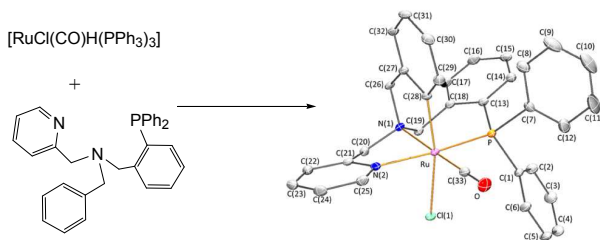
En Route to Chiral-at-Metal Ruthenium Complexes Containing Tripodal Tetradentate Ligands

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Ruthenium(II) complexes bearing tripodal tetradentate ligands



ABSTRACT: Tripodal ligands **LH1-LH3** diastereoselectively react with the dimer $[\{(\text{Cy})\text{RuCl}\}_2(\mu\text{-Cl})_2]$ ($\text{Cy} = \eta^6\text{-}p\text{-MeC}_6\text{H}_4i\text{Pr}$) affording the *p*-cymene compounds $[(\text{Cy})\text{Ru}(\kappa^3N,N',P\text{-LH})][\text{SbF}_6]_2$ (**LH** = **LH1** (**1**), **LH2** (**2**), **LH3** (**3**)) as a racemic mixture of only the R^*_{Ru}, S^*_N isomers. Refluxing in MeCN complexes **1-3** gives racemates of a *fac* isomer of the complexes $[\text{Ru}(\kappa^3N,N',P\text{-LH})(\text{NCMe})_3][\text{SbF}_6]_2$ (**LH** = **LH1** (**4a**), **LH2** (**5a**), **LH3** (**6a**)). In refluxing MeOH, isomers **4a-6a** evolve to the corresponding *mer* isomers **4c-6c**. Reaction of $[\text{RuCl}_2(\text{PPh}_3)_3]$ with **LH1** affords $[\text{RuCl}_2(\text{PPh}_3)(\kappa^3N,N',P\text{-LH1})]$ (**7**) as a racemic mixture of only one pair of stereoisomers. $[\text{RuClH}(\text{CO})(\text{PPh}_3)_3]$ reacts with **LH** to give $[\text{RuH}(\text{CO})(\text{PPh}_3)(\kappa^3N,N',P\text{-LH})]$.

LH)]Cl (LH = LH1 (8), LH2 (9), LH3 (10)) in which the **LH** ligands present a κ^3 coordination mode. Complexes **8-10** were isolated as a mixture of only two diastereomers as pairs of enantiomers. Refluxing in 2-ethoxyethanol suspensions of mixtures of isomers of the complexes **8-10** afforded the corresponding metalated complexes $[\text{RuCl}(\text{CO})(\kappa^4\text{C},\text{N},\text{N}',\text{P}-\text{L})]$ (**L** = **L1** (**11**), **L2** (**12**), **L3** (**13**)). Only one stereoisomer was detected for complexes **11** and **13** but metalation at the C-2 or C-6 carbons gave a mixture of two isomers for complex **12**. The new complexes have been characterized by analytical and spectroscopic means and by the determination of the crystal structures of the complexes **1**, **2**, **5c**, **10a**, **11a**, **12a,b** and **13a** by X-ray diffractometry.

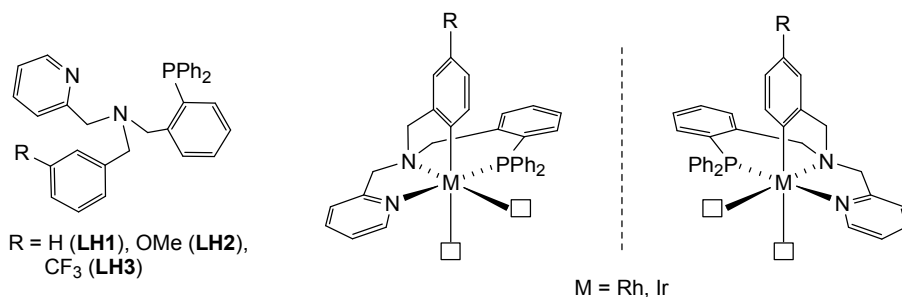
INTRODUCTION

Typically, an asymmetric metallic catalyst consists of a metal surrounded by a chiral ligand together with some ancillary achiral ligands. Activation of prochiral substrates takes place through coordination to the metal and during the catalytic process chirality is transferred from the catalyst to the newly formed stereogenic centers.¹ According to this path, it might be argued that chiral-at-metal catalysts would be well suited to transfer chirality efficiently due to the close proximity between the source and the receptor of chirality.²

However, examples of chiral catalysts in which the source of chirality was unequivocally the stereogenic metal center are scarce. Most probably, this scantiness is due to the demanding requirements of resolution, configurational stability and labile coordination sites that make the design of these peculiar species a challenging task. Indeed, efficient chiral-at-metal catalysts bearing solely achiral ligands have been developed only recently. The contribution of Meggers's group to this area is especially relevant.^{2a,3} The new class of catalysts prepared by this group mostly consist of cationic octahedral rhodium(III), iridium(III) or, in a lesser extent, ruthenium(II) complexes containing two cyclometalated 5-*tert*-butyl-2-phenylbenzoxazoles, 5-*tert*-butyl-2-phenylbenzothiazoles or *N*-(2-pyridyl)-*N*-heterocyclic carbene and two labile acetonitrile molecules. Chirality results from the right-handed (Δ) or left-handed (Λ) propeller defined by the two cyclometalated ligands. The resulting compounds are efficient asymmetric catalysts for a variety of transformations including visible-light-activated photoredox reactions.^{2a,3}

In this regard, we have recently shown that, in octahedral rhodium(III) and iridium(III) complexes, tripodal ligands (**LH**) of the type depicted in Chart 1 are able to act as tetradentate ligands through the aminic and pyridinic nitrogen atoms, the

phosphorus and one of the aromatic carbon atoms of the benzyl substituent. Remarkably, when in octahedral complexes, tripodal ligands display a κ^4C,N,N',P coordination mode, the presence of four distinct ligating atoms guarantees the stereogenicity at the metal as well as the mutual *cis* disposition of the two remaining coordination sites, which are potentially available for catalytic transformations.



Scheme 1. Octahedral rhodium and iridium complexes with tripodal tetradentate ligands showing a κ^4C,N,N',P coordination mode.

It is worthy of note that steric and electronic constraints within this type of ligands controls the stereochemistry of the complexes. Thus, experimental studies and DFT calculations showed that the isomer in which the phosphorus atom is *trans* to the pyridinic nitrogen (see Scheme 1) is the most stable and, indeed, it was the only detected and isolated.⁴ On the other hand, starting from the aminic **LH** ligands, the compounds will be obtained as racemic mixtures containing the metal and the aminic nitrogen as stereogenic centers. Notably, the sign of the chirality adopted by the metal predetermines the configuration at the aminic nitrogen⁵ and it has been shown that the coordination features of the tetradentate ligands confer a high thermal and configurational stability to the 4d and 5d metal complexes.⁴

We have recently resolved the dichlorido rhodium racemates $[\text{RhCl}_2(\kappa^4C,N,N',P\text{-}\mathbf{L1})]$ and applied derived enantiopure solvates $[\text{RhCl}(\kappa^4C,N,N',P\text{-}\mathbf{L1})(\text{Solv})]^+$ (Solv = H_2O , MeCN) or $[\text{Rh}(\kappa^4C,N,N',P\text{-}\mathbf{L1})(\text{NCMe})_2]^{2+}$ as catalyst precursors in the Diels-Alder reaction between methacrolein and cyclopentadiene. Enantiomeric ratios of up to > 99/1 were obtained.⁶ In this regard, it is

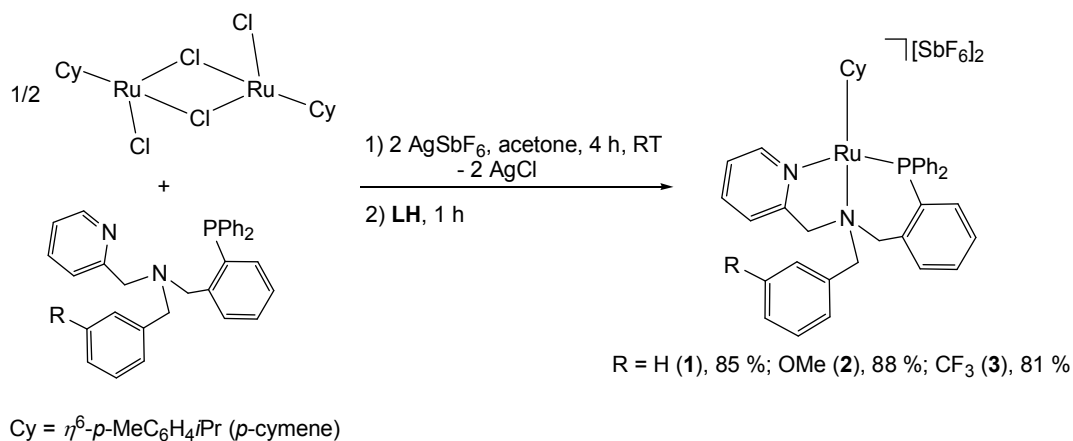
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3 pertinent to point out that the phenyl groups of the phosphano arm of the ligand **L1**
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5 shield one of the faces of the coordination plane defined by the metal and the two vacant
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7 sites. However, the other face of this plane remains essentially clear. This property, that
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9 is a general feature for this type of complexes,^{4,6} is on the basis of the high
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11 enantioselectivity achieved and, hence, the fruitful application of this type of catalysts to
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13 related enantioselective transformations may be anticipated.
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16 Taken into account all these considerations, here we present our attempts to prepare
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18 octahedral ruthenium(II) complexes bearing the tripodal tetradentate ligands **LH** (Chart
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20 1) displaying a κ^4C,N,N',P coordination mode. Their optical resolution and catalytic
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22 applications will be reported in due course.
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RESULTS AND DISCUSSION

The ligands **LH1-LH3** (Chart 1) were prepared as previously reported.^{4a} The synthesis of ruthenium complexes was attempted starting from the *p*-cymene dimer $[\{(\text{Cy})\text{RuCl}\}_2(\mu\text{-Cl})_2]$ ($\text{Cy} = \eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr}$)⁷ as well as from the monomers $[\text{RuCl}_2(\text{PPh}_3)_3]$ ⁸ and $[\text{RuClH}(\text{CO})(\text{PPh}_3)_3]$.⁹

Reactions starting from $[\{(\text{Cy})\text{RuCl}\}_2(\mu\text{-Cl})_2]$. Treatment of acetone solutions of the dimer $[\{(\text{Cy})\text{RuCl}\}_2(\mu\text{-Cl})_2]$ with AgSbF_6 , removal of the AgCl formed and subsequent addition of the corresponding ligand **LH** afforded complexes of formula $[(\text{Cy})\text{Ru}(\kappa^3\text{N},\text{N}',\text{P}\text{-}\mathbf{LH})][\text{SbF}_6]_2$ (**LH** = **LH1** (**1**), **LH2** (**2**), **LH3** (**3**)) in 81-88 % yield (Scheme 2).



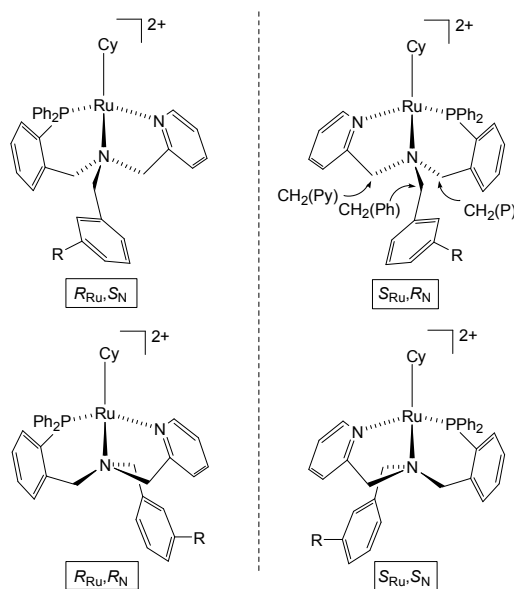
$\text{Cy} = \eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr}$ (*p*-cymene)

Scheme 2. Synthesis of complexes **1-3**.

Scheme 3 shows the two diastereomers as pairs of enantiomers of compounds **1-3** that could form in the reaction. The NMR spectra of the isolated solids consist of only one set of sharp signals from RT to 193 K. Therefore, we propose that the formation of these complexes is completely diastereoselective.

The compounds were characterized by analytical and spectroscopic methods (see Experimental) and by the X-ray determination of the crystal structures of complexes **1** and **2**. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the isolated isomers consists of one singlet near to 40 ppm. The three methylene groups of protons are diastereotopic. The value of the

$J(\text{PH})$ coupling constant together with COSY, HSQC and HMBC experiments permit the assignment of these protons which have been labeled as $\text{CH}_2(\text{Py})$, $\text{CH}_2(\text{Ph})$ and



Scheme 3. Isomers of the complexes $[(\text{Cy})\text{Ru}(\kappa^3\text{N},\text{N}',\text{P-LH})]^{2+}$ (**1-3**).

$\text{CH}_2(\text{P})$ (see Scheme 3). One of the $\text{CH}_2(\text{Ph})$ methylene protons shows NOE cross peaks with the protons of one of the methyl groups of the isopropyl substituent of the cymene ligand. However, no NOE interaction has been observed between the $\text{CH}_2(\text{P})$ methylene protons and any of the *p*-cymene protons. These NOE data are only compatible with the pair of enantiomers $R^*_{\text{Ru}}, S^*_{\text{N}}$.¹⁰

Single crystals of **1** and **2**, suitable for X-ray analysis, were obtained from CH_2Cl_2 /pentane solutions. As at a molecular level both structures present similar parameters we will discuss here only the structural features of complex **1**. For the structural data of complex **2**, see SI. The complex crystallizes in the $P\bar{1}$ centrosymmetric space group and, therefore, a pair of enantiomers, specifically the $R_{\text{Ru}}, S_{\text{N}}$ and $S_{\text{Ru}}, R_{\text{N}}$ isomers¹⁰ (see Scheme 3), is present in its unit cell. These absolute configurations correspond to those found spectroscopically for the isolated solid. A view of the structure of the cation of $(S_{\text{Ru}}, R_{\text{N}})$ -**1** is depicted in Figure 1 and relevant characteristics of the metal coordination sphere are summarized in Table 1.

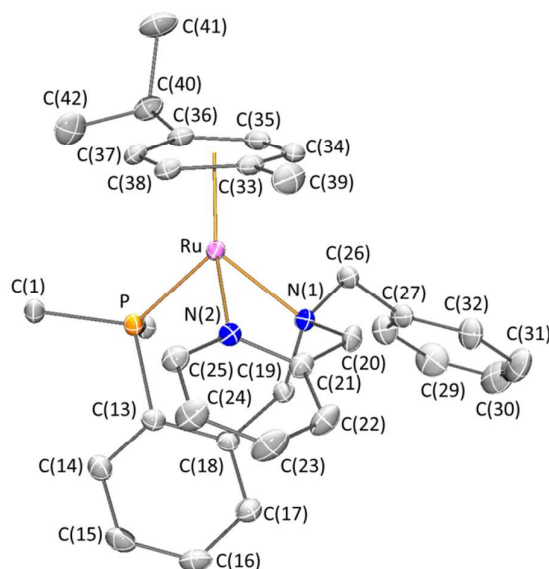


Figure 1. Molecular structure of the cation of the (S_{Ru}, R_N)-**1** isomer. For clarity, hydrogen atoms have been omitted and only the *ipso* carbon atoms of PPh_2 group have been included.

Table 1. Selected Bonds Lengths (Å) and Angles (°) for the Complex (S_{Ru}, R_N)-1****

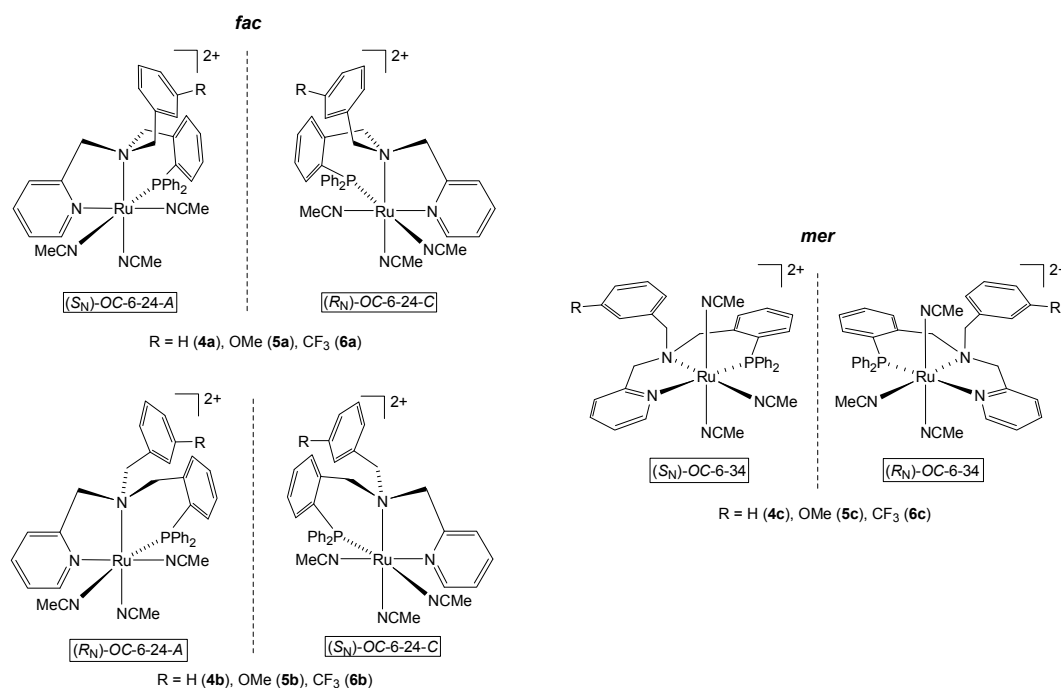
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|--------------------|------------|--------------|-----------|
| Ru-P | 2.3503(6) | P-Ru-N(2) | 90.34(5) |
| Ru-N(1) | 2.2144(17) | P-Ru-Ct | 132.14(1) |
| Ru-N(2) | 2.0855(17) | N(1)-Ru-N(2) | 76.19(7) |
| Ru-Ct ^a | 1.7712(1) | N(1)-Ru-Ct | 130.94(1) |
| P-Ru-N(1) | 87.03(5) | N(2)-Ru-Ct | 122.54(1) |

^aCt is the centroid of the arene ring of *p*-cymene ligand.

The ruthenium is pseudo-tetrahedral being coordinated to an η^6 -Cy ring and to the phosphorus, aminic nitrogen and pyridinic nitrogen of the ligand **LH1**. The axis of the Cy ligand is roughly parallel to the vector connecting P and N(2), avoiding the steric effects of the CH_2Ph fragment bound to N(1). Ruthenium–nitrogen bond lengths are dissimilar, with an elongation of Ru–N(1) (aminic nitrogen) bond length, compared to Ru–N(2) (pyridinic nitrogen) ($\Delta(Ru-N)$: 0.129(2) Å) slightly longer than that observed in the related complex $[RhCl_3(\kappa^3N, N', P-L1)]$ complex ($\Delta(Rh-N)$: 0.112(2) Å).^{4a}

When acetonitrile solutions of the complexes **1-3** were heated at 65 °C for 48 h, the Cy ligand was removed and complexes of formula $[Ru(\kappa^3N, N', P-LH)(NCMe)_3][SbF_6]_2$ (**LH** = **LH1** (**4**), **LH2** (**5**), **LH3** (**6**)) were recovered from the reaction medium.

In these complexes, the metal and the aminic nitrogen are stereogenic centers. All the possible isomers of complexes **4-6**—two enantiomeric pairs of *fac* and an enantiomeric pair of *mer* isomers—are depicted in Scheme 4 labeled with their corresponding stereochemical descriptors.^{10a,b,11}



Scheme 4. Isomers of the complexes $[\text{Ru}(\kappa^3\text{N},\text{N}',\text{P-LH})(\text{NCMe})_3]^{2+}$ (**4-6**).

Complexes **4-6** were characterized by analytical and spectroscopic means (see Experimental). Assignment of the NMR signals was accomplished by two-dimensional homonuclear and heteronuclear correlations. At room temperature, the ^1H and ^{31}P NMR spectra consist of only one set of sharp signals. Besides the three methylene groups of diastereotopic protons, the ^1H NMR spectra show three singlets around 2.5 ppm, attributed to three inequivalent NCMe groups, together with a deshielded doublet centered about 8.45 ppm assigned to the proton in the 6-position of the pyridine moiety (6-CH(Py)). Interestingly, whereas the latter shows no coupling to the phosphorus, one of the NCMe nitrile carbon atoms presents a $J(\text{CP})$ coupling constant of around 14.5 Hz, as expected for a *trans* disposition between the NCMe and PPh_2 fragments.

Inspection of molecular models indicates that in the *fac* isomers **4b-6b** there is steric hindrance between the benzyl and two phosphine phenyls substituents of the ligand **L** (Scheme 4). Taking into account this observation, the NMR data suggest that the isolated solids are the *fac* isomers **4a-4b**.

At 193 K, the ^1H and ^{31}P NMR spectra of the isolated solids showed two set of signals. In particular, at this temperature, the ^{31}P NMR spectra consist of two singlets at about 53 and 51-52 ppm in about 87/13 molar ratio, respectively, which coalesce to one unique singlet by heating the sample. The coalescence of these two sets of NMR signals under soft experimental conditions can be accounted for by assuming an interchange between two conformers of isomers **4a-6a**. In fact, DFT studies on the related isoelectronic rhodium(III) complexes $[\text{RhCl}_3(\kappa^3\text{N},\text{N}',\text{P}-\text{L1})]$ identified two conformers for the corresponding a isomers depending on the conformation of the six-membered Rh-P-C-C-C-N ring (see Scheme 4).^{4a}

Refluxing in methanol for 48 h complexes **4-6**, new species form according to NMR measurements. Conversion was complete for complexes **4** and **5** but only 40 % of conversion was measured for complex **6**. In the ^{13}C NMR spectra of the new species, no $J(\text{PC})$ coupling was observed for any of the three nitrile carbons present in the molecules. In their ^1H NMR spectra, the signal corresponding to the 6-CH(Py) proton appears as a multiplet derived from $J(\text{HH})$ a $J(\text{PH})$ couplings as it has been elucidated from the $^1\text{H}\{^{31}\text{P}\}$ NMR spectra. These spectroscopic data point to structures in which the pyridine and PPh_2 arms of the **LH** ligand are located mutually *trans*.

To unequivocally establish the structure of the new species, the crystal structure of the compound **5c** was determined by X-ray diffraction means. Crystals suitable for X-ray diffraction studies were grown from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ solutions of the complex. The molecular structure (Figure 2) shows that the ligand **LH2** binds meridionally to the

ruthenium center in a (κ^3N,N',P) fashion. The complex crystallizes in the $P\bar{1}$ centrosymmetric space group and the two enantiomers are present in the unit cell. Inspection of intermolecular interactions evidences the overlap between methyl and benzyl groups of methoxybenzyl fragments of two antipodes as well as the presence of weak C-H \cdots O interactions (see SI).

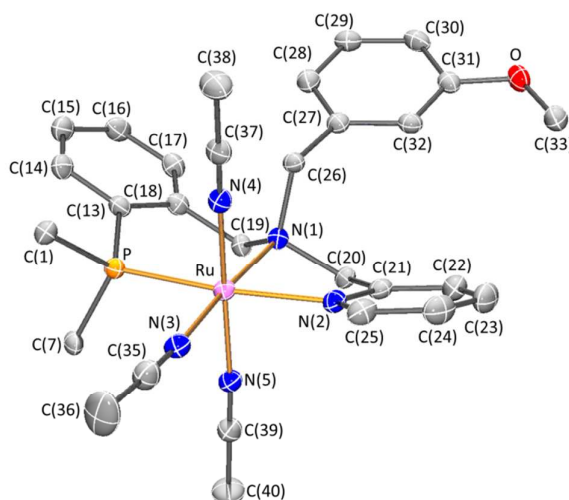


Figure 2. Molecular structure of the cation of the $((R_N)\text{-OC-6-34})\text{-5c}$ isomer. For clarity, hydrogen atoms have been omitted and only the *ipso* carbons of the PPh_2 group are shown.

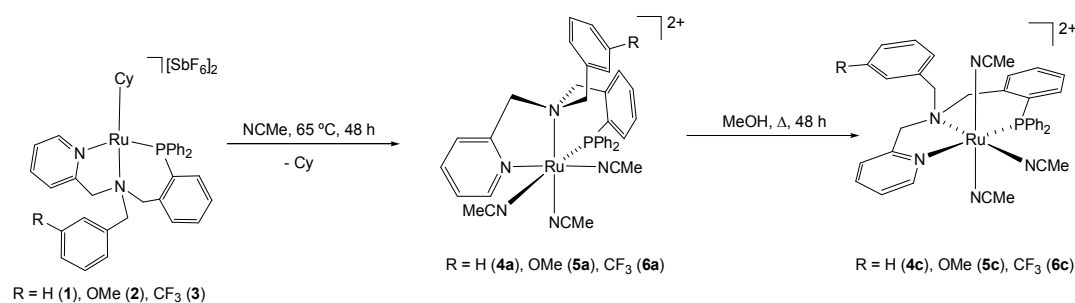
Table 2 collects some structural parameters of the metal coordination sphere. The pseudooctahedral geometry together with the presence of non-bulky linear acetonitrile groups induce a significantly smaller ring puckering amplitude for the Ru-P-C-C-C-N six membered metallacycle, compared to that observed in complex **1** (see SI). The Ru–NCMe bond lengths are similar, ranging from 2.033(3) Å for the Ru–N(3) bond *trans* to the aminic nitrogen, to 2.024(3) and 2.020(3) Å for the Ru–N(4) and Ru–N(5) bonds which are mutually *trans*.

Thus, the new species is the *mer-5c* and, from the similarity of the analytical and spectroscopic data, we propose that the same meridional isomers, *mer-4c* and *mer-6c* (see Scheme 4), were isolated working with the **LH1** and **LH3** ligands, respectively.

Table 2. Selected Bonds Lengths (Å) and Angles (°) for the Complex 5c

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|-----------|------------|--------------|------------|
| Ru-P | 2.2817(10) | N(1)-Ru-N(2) | 78.84(11) |
| Ru-N(1) | 2.153(3) | N(1)-Ru-N(3) | 175.66(12) |
| Ru-N(2) | 2.120(3) | N(1)-Ru-N(4) | 94.54(11) |
| Ru-N(3) | 2.033(3) | N(1)-Ru-N(5) | 88.90(12) |
| Ru-N(4) | 2.020(3) | N(2)-Ru-N(3) | 96.85(12) |
| Ru-N(5) | 2.024(3) | N(2)-Ru-N(4) | 86.72(12) |
| P-Ru-N(1) | 94.09(8) | N(2)-Ru-N(5) | 91.05(12) |
| P-Ru-N(2) | 172.71(9) | N(3)-Ru-N(4) | 85.68(12) |
| P-Ru-N(3) | 90.24(9) | N(3)-Ru-N(5) | 90.67(12) |
| P-Ru-N(4) | 92.14(9) | N(4)-Ru-N(5) | 175.46(12) |
| P-Ru-N(5) | 90.57(9) | | |

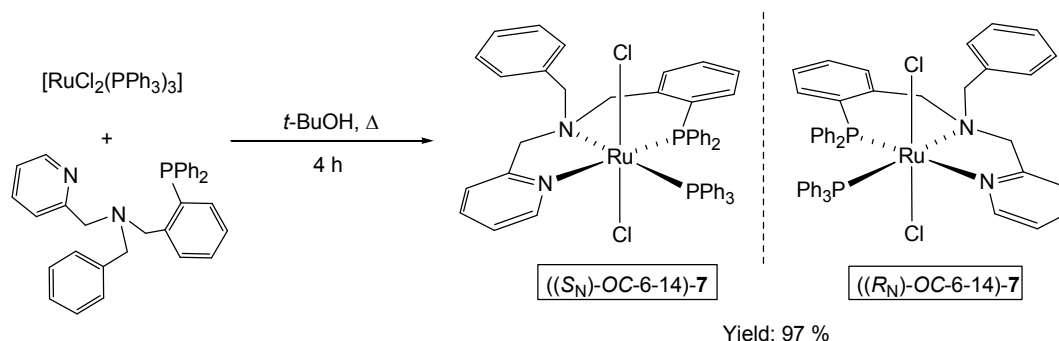
In summary, reaction of complexes **1-3** in refluxing acetonitrile gives rise to the *fac* isomers **4a-6a**. In refluxing methanol, these compounds evolve to the *mer* isomers **4c**, **5c** and **6c** (40 % conversion for complex **6** after 48 h of treatment, Scheme 5).

**Scheme 5.** Synthesis of the *fac* and *mer* isomers of the complexes **4-6**. Only one enantiomer of each pair is shown.

All attempts of metalation of the benzylic arm of the ligands **LH** in complexes **4-6** have been unsuccessful. Thus, no orthometalation products were isolated when the complexes were refluxed in MeOH or EtOH in the presence of various relative amounts of NaAcO or lithium trifluoroacetate (3-5 equiv.) during several hours (up to 2-3 days). Untreatable mixtures of uncharacterized compounds, some of them containing coordinated acetate or trifluoroacetate ligands, were obtained. Heating ethanolic solutions of the starting compounds at higher temperatures (100-120 °C) in sealed tubes mostly led to decomposition.

Reactions starting from [RuCl₂(PPh₃)₃]. Reaction of [RuCl₂(PPh₃)₃] with **LH1** in refluxing *tert*-butanol afforded [RuCl₂(PPh₃)(κ³N,N',P-**LH1**)] (**7**) in 97 % yield

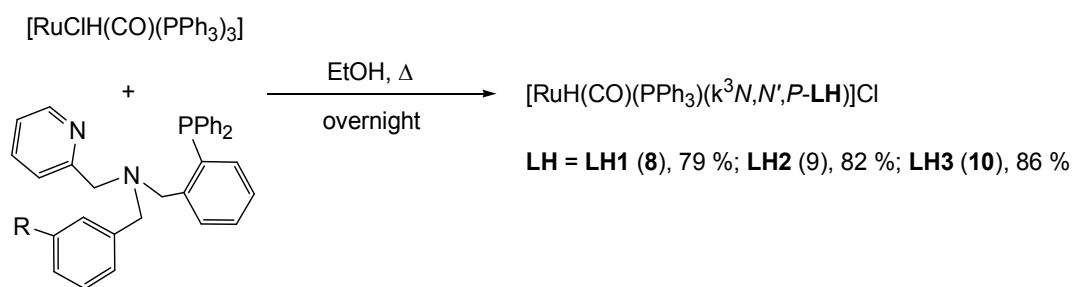
(Scheme 6). The NMR spectra of the isolated solid consist of only one set of sharp signals from RT to 193 K. Therefore, we propose that the formation of this complex is completely diastereoselective. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **7** consist of two doublets centered at 43.34 and 42.27 ppm with a $J(\text{PP}')$ coupling constant of 30.7 Hz attributed to the PPh_3 ligand and to the diphenylphosphino moiety of the **LH1** ligand, respectively. The pattern of $J(\text{HP})$ and $J(\text{CP})$ couplings encountered for **7** (see Experimental) is in agreement with the structure of the pair of enantiomers (S_N)-OC-6-14/(R_N)-OC-6-14 depicted in Scheme 6.



Scheme 6. Synthesis of complex **7**.

When a sample of complex **7** was refluxed in 2-ethoxyethanol for 2 days in the presence of 4 equiv of NaAcO a small portion (about 9 % yield) of the metalated complex $[\text{RuCl}(\text{CO})(\kappa^4\text{C},N,N',P\text{-L1})]$ (**11**) was obtained. For an improved synthesis of **11** and its characterization see below.

Reactions starting from $[\text{RuClH}(\text{CO})(\text{PPh}_3)_3]$. A 1/1 mixture of $[\text{RuClH}(\text{CO})(\text{PPh}_3)_3]$ and **LH** was suspended in ethanol and refluxed overnight to give, in 79-86 % yield, the corresponding complex of formula $[\text{RuH}(\text{CO})(\text{PPh}_3)(\kappa^3N,N',P\text{-LH})]\text{Cl}$ (**LH** = **LH1** (**8**), **LH2** (**9**), **LH3** (**10**)) according to elemental analysis and mass spectrometry measurements (Scheme 7).



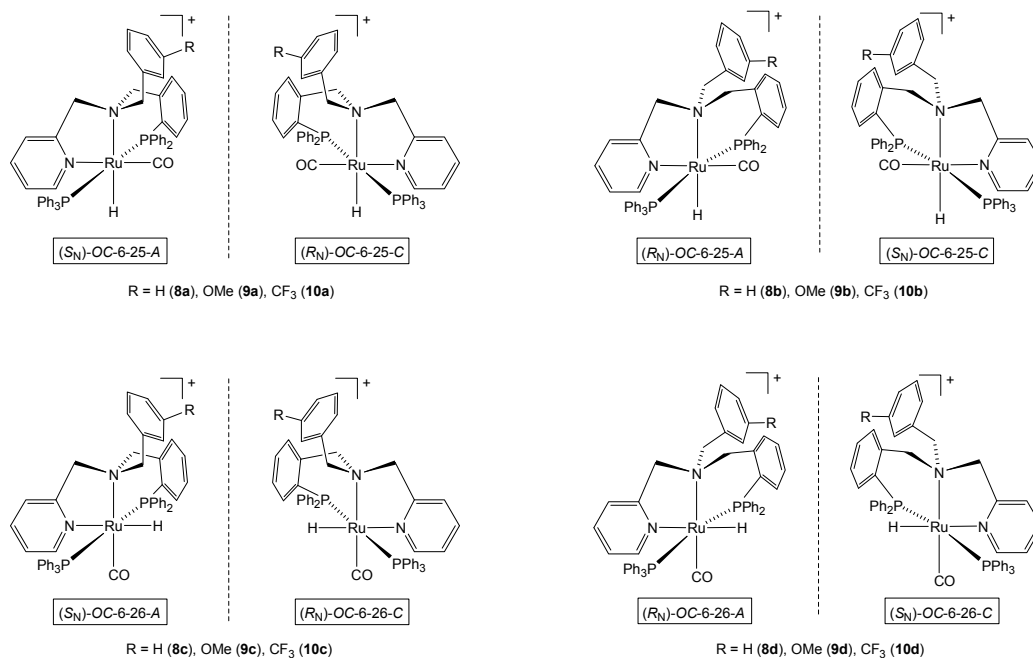
Scheme 7. Synthesis of complexes **8-10**.

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At 213 K, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the isolated solids in methanol- d_4 consist of two AB and one AX systems with a coupling constant of about 255 Hz for all the three ^{31}P spin systems. These data indicate the presence of three different species and the value of the coupling constants suggests that the two phosphorus atoms present in the three species are *trans* to each other. At the same temperature, in the hydrido region of the ^1H NMR spectra, two double doublets and a pseudo triplet, in *ca.* 2.5/24.5/73 intensity ratio were observed. Coupling constants in the range 14-29 Hz were determined for these multiplets indicating that a hydrido ligand is located *cis* with respect to two phosphorus nuclei. Consistently, at 298 K, in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, the CO carbon of compounds **9** and **10** appears as a pseudo triplet due to two almost equal *cis* $J(\text{PC})$ constants of about 16 Hz.

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From the 36 possible stereoisomers (18 pairs of enantiomers) for an octahedral geometry like that of complexes **8-10**, namely, $\text{RuABC}(\kappa^3\text{N},\text{N}',\text{P-D})$ with one of the nitrogen atoms being stereogenic, only the four pairs of enantiomers depicted in Scheme 8 fulfill all the NMR data above mentioned.



Scheme 8. Possible stereochemistries of the isolated isomers of complexes **8-10**.

Single crystals of complex **10a** have been obtained from dichloromethane solutions. A view of the molecular structure is depicted in Figure 3 and relevant characteristics of the metal coordination sphere are summarized in Table 3.

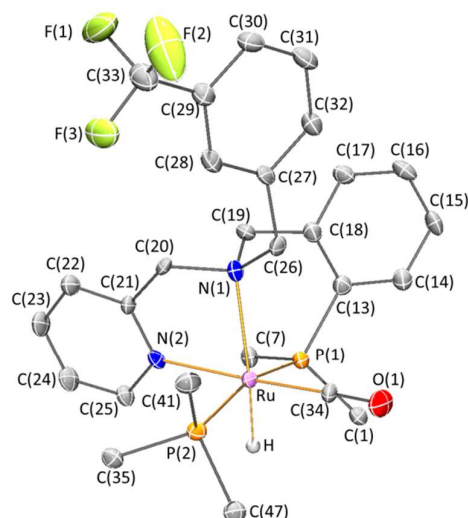


Figure 3. Molecular structure of the cation of the ((S_N)-OC-6-25-A)-**10a** isomer. For clarity, hydrogen atoms (except the hydride) have been omitted and only the *ipso* carbons of the PPh₂ and PPh₃ groups are shown.

Table 3. Selected Bonds Lengths (Å) and Angles (°) for the Complex 10a

| | | | |
|---------------|------------|---------------|------------|
| Ru-P(1) | 2.3379(10) | P(2)-Ru-N(1) | 103.78(8) |
| Ru-P(2) | 2.3798(9) | P(2)-Ru-N(2) | 89.20(8) |
| Ru-N(1) | 2.285(3) | P(2)-Ru-C(34) | 88.51(13) |
| Ru-N(2) | 2.149(3) | P(2)-Ru-H | 83.2(18) |
| Ru-C(34) | 1.829(3) | N(1)-Ru-N(2) | 75.83(10) |
| Ru-H | 1.47(5) | N(1)-Ru-C(34) | 100.73(13) |
| P(1)-Ru-P(2) | 164.91(3) | N(1)-Ru-H | 169.1(19) |
| P(1)-Ru-N(1) | 91.29(8) | N(2)-Ru-C(34) | 175.29(14) |
| P(1)-Ru-N(2) | 93.66(8) | N(2)-Ru-H | 96.1(19) |
| P(1)-Ru-C(34) | 89.61(13) | C(34)-Ru-H | 87.7(19) |
| P(1)-Ru-H | 81.8(19) | | |

The complex exhibits a distorted-octahedral coordination environment with the ruthenium atom bonded in a *fac* fashion to the phosphorus (P(1)) and the aminic (N(1)) and pyridinic (N(2)) nitrogen atoms of the **LH3** ligand. A PPh₃, a hydride and a CO ligand, *trans* to the P(1), N(1) and N(2) atoms, respectively, complete the coordination sphere around the metal. The complex crystallizes in the $P\bar{1}$ centrosymmetric space group and therefore its unit cell ($Z = 2$) contains a pair of enantiomers of **10a**, specifically the (*S_N*)-*OC*-6-25-*A* and (*R_N*)-*OC*-6-25-*C*^{10a,b,11} isomers. The strong trans influence of the hydrido ligand leads to an elongation of the Ru-N(1) bond (2.285(3) Å) whose value is significantly longer than those of the Ru-N(amine) bond lengths in complexes **1** (2.2144(17) Å) and **5c** (2.153(3) Å). On the contrary, both Ru-P bond lengths are similar, and close to those reported in octahedral Ru complexes with phenyl phosphine groups *trans* to each other (mean Ru-P bond length: 2.34(2) Å).¹²

At 213 K, the metal-hydrido region of the ¹H NMR spectrum consists of a pseudo triplet and a double doublet in *ca.* 75/25 molar ratio (Figure 4). The double doublet corresponding to the less abundant species (213 K, about 2 %, $\delta_{\text{H}} = -11.05$, $J(\text{PH}) = 24.1, 17.3$ Hz) was not detected. Hence, the equilibrium between the two major species is quickly achieved even at low temperature. Heating up the solution, these signals broaden out, coalesces at about 271 K resulting in a sharp pseudo triplet at 313 K. The process obeys a first-order rate law, with derived activation parameters at 293 K of ΔH^\ddagger

$= -0.83 \pm 0.04 \text{ kcal} \cdot \text{mol}^{-1}$, $\Delta S^\ddagger = -44.4 \pm 5.8 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ and $\Delta G^\ddagger = 12.19 \pm 1.75 \text{ kcal mol}^{-1}$ (see Supporting Information).

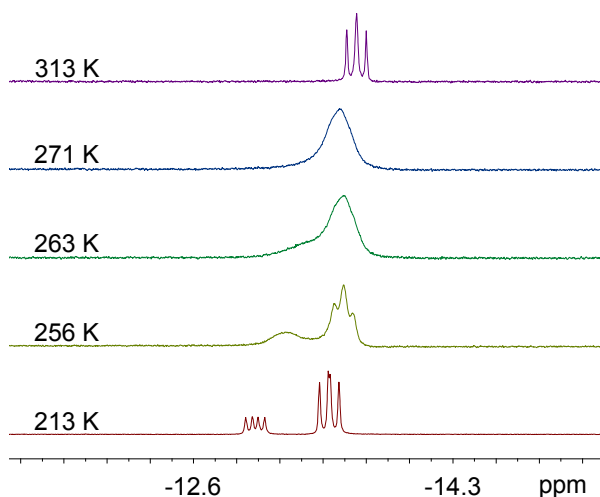


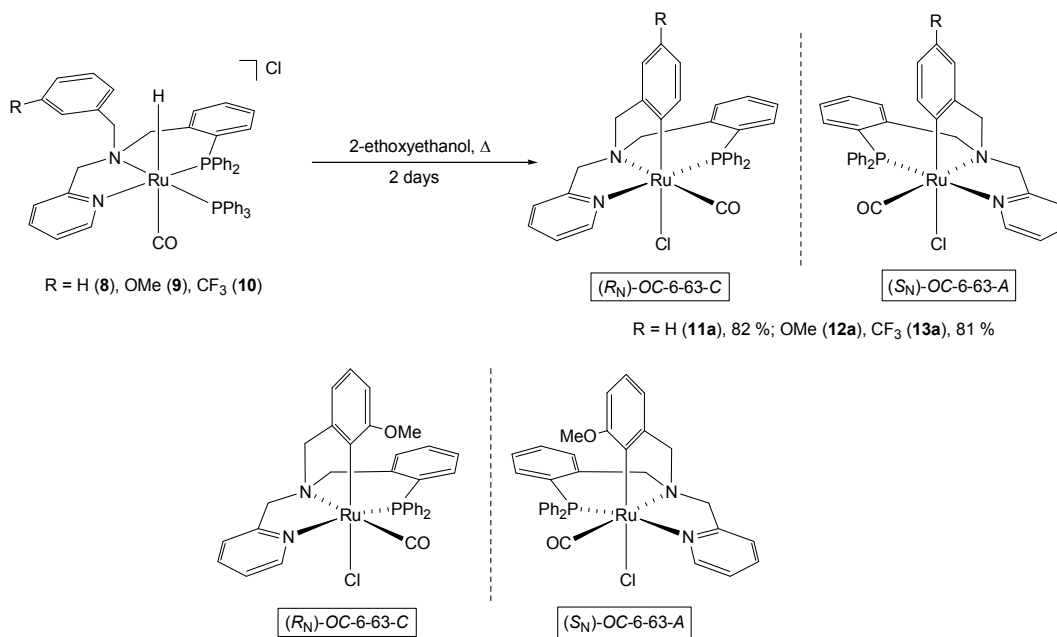
Figure 4. Evolution with the temperature of the hydrido region of the ^1H NMR spectra of complexes **10**.

Taking into account the low value of the involved barrier, we tentatively propose that the observed fluxional process is due to an equilibrium between two conformers of the stereoisomers **10a**. As mentioned before, for related *fac* isomers of the rhodium(III) complexes $[\text{RhCl}_3(\kappa^3N,N',P\text{-}\mathbf{L1})]$, DFT calculations located two conformations for the six-membered Rh-P-C-C-C-N ring (see Scheme 8) that equilibrates fast at room temperature.^{4a}

In summary, the reaction of $[\text{RuClH}(\text{CO})(\text{PPh}_3)_3]$ with the tripodal ligands **LH** is highly diastereoselective affording high yields of a mixture of only two diastereomers. The major isomers, **8a-10a**, were obtained in about 97.5/2.5 diastereomeric relation.

Refluxing in 2-ethoxyethanol for 2 days suspensions of mixtures of isomers of the complexes $[\text{RuH}(\text{CO})(\text{PPh}_3)(\kappa^3N,N',P\text{-}\mathbf{LH})]\text{Cl}$ (**8-10**) afforded the corresponding metalated complexes $[\text{RuCl}(\text{CO})(\kappa^4C,N,N',P\text{-}\mathbf{L})]$ (**L** = **L1** (**11**), **L2** (**12**), **L3** (**13**)). Monitoring the reaction by NMR, the only detected compounds, under the reaction

conditions, were the starting mixture of compounds **8-10** and the isolated metalated complexes **11-13**.



Scheme 9. Synthesis of the complexes **11-13**.

Taking into account that metalation of the methoxy and trifluoromethyl substituted ligands **LH2** and **LH3** could take place at the C-2 or at C-6 carbons of the benzyl arm, up to 12 diastereomers as pairs of enantiomers of complexes **12** and **13** could form (6 pairs in the case of complex **11** derived from the unsubstituted **LH1** ligand). However, whereas for the methoxy derivative metalation was observed at the two possible positions, for the trifluoromethyl derivative only metalation at C-6 carbon occurred. The preparative route is highly selective: only the diastereomers **11a** and **13a** were detected for complexes **11** and **13**. For complex **12**, metalation occurs at the C-2 or at C-6 carbon and two diastereomers, **12a** and **12b**, were isolated (Scheme 9).

The complexes have been characterized by analytical and spectroscopic methods and by the X-ray determination of their crystal structures. The three groups of diastereotopic methylene protons, labeled as CH₂(Py), CH₂(Ph) and CH₂(P), have been

assigned through mono- and bi-dimensional homo- and hetero-nuclear NMR experiments. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra consist of a singlet at *ca.* 56 ppm, about 16 ppm downfield shifted with respect to the PPh_2 signal of the starting compounds. A ^{13}C resonance in the range 154-178 ppm, showing a typical *cis* $J(\text{PC})$ coupling constant of about 11 Hz, indicates the presence of a $\text{Ru}-\text{C}(\text{sp}^2)$ bond. The value of the $J(\text{PC})$ coupling constant of the carbonyl carbon, around 18 Hz, also indicates a *cis* arrangement between the CO and PPh_2 groups. The 6-CH proton of the pyridine moiety shows a $J(\text{PH})$ coupling indicating a *trans* disposition with respect to the PPh_2 group. All these data together support the geometry depicted in Scheme 8 for complexes **11-13**.

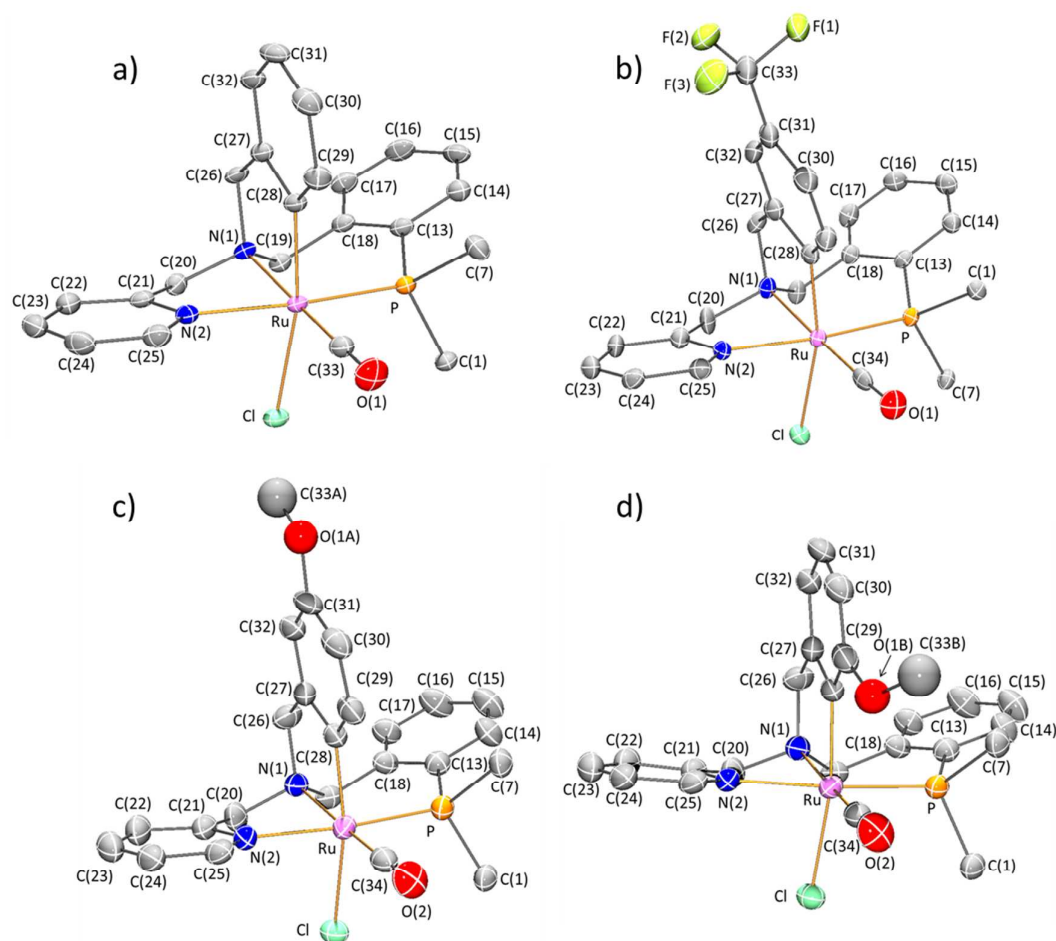


Figure 5. Molecular structure of the complexes a) ((*R*_N)-OC-6-63-C)-**11a**, b) ((*R*_N)-OC-6-63-C)-**13a**, c) ((*R*_N)-OC-6-63-C)-**12a** and d) ((*R*_N)-OC-6-63-C)-**12b**. For clarity hydrogen atoms have been omitted and only *ipso* carbon atoms of phenyl groups have been included.

In order to unequivocally ascertain the structure of the metalated compounds, the crystal structures of complexes **11**, **12a,b** and **13** have been determined by X-ray diffraction. The crystal structure of complex **12** reveals the existence of a disorder between **12a** and **12b** isomers with a 0.765/0.235(5) proportion. A view of the molecular structure of the three complexes (including both isomers of complex **12**) is depicted in Figure 5 and the structural parameters of the metal coordination spheres are listed in Table 4.

Table 4. Selected Bond Lengths (Å) and Angles (°) for the Complexes 11a, 12a,b, and 13a

| | 11a | 12a,b | 13a |
|-----------------------------------------|------------|--------------|------------|
| Ru-Cl | 2.5070(8) | 2.5314(12) | 2.5316(13) |
| Ru-P | 2.2857(8) | 2.2954(13) | 2.2918(12) |
| Ru-N(1) | 2.186(2) | 2.180(4) | 2.175(4) |
| Ru-N(2) | 2.128(3) | 2.131(4) | 2.134(4) |
| Ru-C(28) | 2.040(3) | 2.047(4) | 2.041(5) |
| Ru-C _(CO) ^a | 1.834(3) | 1.838(6) | 1.859(5) |
| Cl-Ru-P | 95.25 (3) | 92.68(4) | 94.49(4) |
| Cl-Ru-N(1) | 88.98(7) | 87.35(10) | 88.59(12) |
| Cl-Ru-N(2) | 84.15(7) | 88.05(10) | 85.29(11) |
| Cl-Ru-C(28) | 168.50(9) | 167.57(13) | 166.30(14) |
| Cl-Ru-C _(CO) ^a | 94.70(10) | 97.51(14) | 95.09(15) |
| P-Ru-N(1) | 92.44(7) | 93.24(11) | 93.03(11) |
| P-Ru-N(2) | 171.51(8) | 171.75(12) | 171.61(12) |
| P-Ru-C(28) | 92.44(8) | 93.33(13) | 96.29(13) |
| P-Ru-C _(CO) ^a | 89.95(10) | 89.46(15) | 88.22(15) |
| N(1)-Ru-N(2) | 79.10(10) | 78.58(15) | 78.58(16) |
| N(1)-Ru-C(28) | 82.14(11) | 81.46(17) | 82.44(19) |
| N(1)-Ru-C _(CO) ^a | 175.42(12) | 174.33(17) | 176.02(19) |
| N(2)-Ru-C(28) | 86.98(11) | 84.46(16) | 82.81(17) |
| N(2)-Ru-C _(CO) ^a | 98.54(12) | 98.59(18) | 100.15(18) |
| C(28)-Ru-C _(CO) ^a | 93.85(13) | 93.41(19) | 93.7(2) |

^a C_(CO) corresponds to C(33) in **11a** and C(34) in **12a,b** and **13a**.

Their molecular structure illustrated distorted-octahedral coordination geometries around the central metal atom. One chlorido and one carbonyl ligand occupy two *cis* coordination sites and the four donating atoms of the tripodal tetradentate ligand complete the metal coordination sphere. As indicated by solution NMR data, the phosphorus atom is *trans* to the pyridinic nitrogen N(2), while the chlorido is found to be *trans* to the aromatic C(28) atom and the CO ligand is *trans* to the aminic nitrogen N(1). The aminic nitrogen and the metal are stereogenic centers. The crystal structure of

the three complexes contains an inversion center and, therefore, the enantiomeric pairs of diastereomers **11a**, **12a,b** and **13a** (see Scheme 8) are present in their unit cells.

Taking into account the potential application of these compounds as catalyst precursors in asymmetric transformations, it is interesting to point out that the phenyl groups of the phosphano arm of the ligand **L** shields one of the faces of the coordination plane containing the chlorido and carbonyl ligands (Figure 6). However, the other face of this plane remains essentially clear. Hence, if a prochiral planar chelate replaces these ligands, one of its enantiofaces would be better shielded than the other and, therefore, enantioselective attacks would be anticipated.

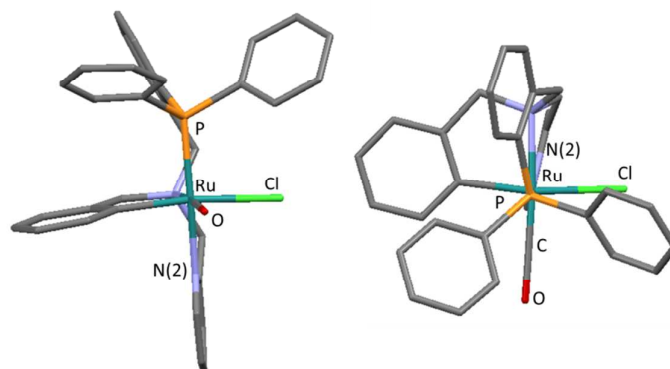


Figure 6. Views of isomer **11a**, (R_N)-OC-6-63-C, along the OC-Ru and P-Ru directions. Similar projections are obtained for complexes **12a**, **12b** and **13a**.

CONCLUSIONS

Ligands **LH1-LH3** react with the ruthenium compounds [$\{(\text{Cy})\text{RuCl}\}_2(\mu\text{-Cl})_2$], $[\text{RuCl}_2(\text{PPh}_3)_3]$ or $[\text{RuClH}(\text{CO})(\text{PPh}_3)_3]$ affording tricoordinate k^3N,N',P complexes of $d^6 \text{Ru}^{2+}$ ions of general formula $[\text{RuABC}(\kappa^3N,N',P\text{-LH})]^{n+}$ in which A, B and C represent *p*-cymene or three equal or different, anionic or neutral, monodentate ligands. In these complexes, the metal and aminic nitrogen atoms are stereogenic centers. All the preparative routes investigated are highly diastereoselective: from the total number of possible isomers that could form, only a reduced number have been detected in each case. Metalated complexes of formula $[\text{RuCl}(\text{CO})(\kappa^4C,N,N',P\text{-L})]$ have been isolated starting from neutral compounds of formula $[\text{RuClH}(\text{CO})(\kappa^3N,N',P\text{-LH})]$. Probably, the presence of a carbonyl group (a strong π -acceptor ligand) facilitates the orthometalation process. Again, the synthesis is stereoselective: only one diastereomer was detected for the ligands **L1** and **L3** but two, derived from metalation at the C-2 or C-6 carbon of the benzylic arm, for the ligand **L2**.

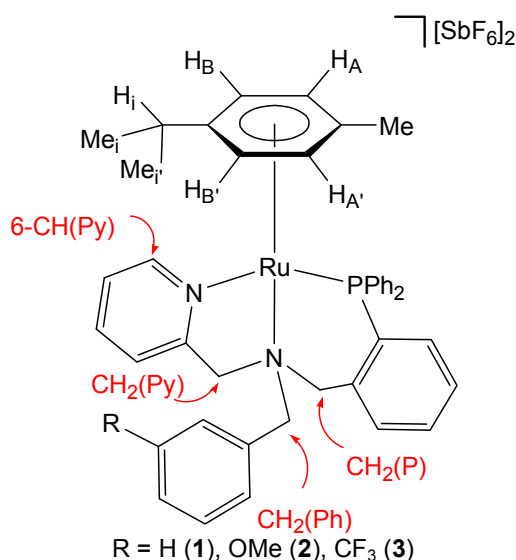
Notably, the asymmetry generated by the stereogenic centers present in the metalated molecules makes the equatorial plane, defined by the metal and the two ligating atoms of the auxiliary ligands Cl and CO, stereochemically differentiated. Consequently, these metalated compounds are potentially good starting materials for the preparation of enantioselective catalysts after optical resolution. We are currently making efforts in this line in our laboratory.

EXPERIMENTAL SECTION

General Information

All preparations have been carried out under argon, unless otherwise stated. All solvents were treated in a PS-400-6 Innovative Technologies Solvent Purification System (SPS) and degassed prior to use. Carbon, hydrogen and nitrogen analyses were performed using a Perkin-Elmer 240 B microanalyzer. ^1H , ^{13}C , ^{31}P and ^{19}F spectra were recorded on a Varian UNITY 300, a Bruker AV-300, a Bruker AV-400 or a Bruker AV-500 spectrometers. Chemical shifts are expressed in ppm up field from SiMe_4 , 85% H_3PO_4 (^{31}P) or CFCl_3 (^{19}F). J values are given in Hz. COSY, NOESY, HSQC, HMQC, and HMBC ^1H -X ($X = ^1\text{H}$, ^{13}C , ^{31}P) correlation spectra were obtained using standard procedures. Infrared spectra were recorded on a Perkin-Elmer Spectrum One FT IR spectrophotometer. Mass spectra were obtained with a Micro ToF-Q Bruker Daltonics spectrometer.

Preparation and characterization of the complexes $[(\text{Cy})\text{Ru}(\kappa^3\text{N},\text{N}',\text{P}-\text{LH})][\text{SbF}_6]_2$ ($\text{LH} = \text{LH1}$ (1**), LH2 (**2**), LH3 (**3**)).** To a solution of the ruthenium dimer $[\{(\text{Cy})\text{RuCl}\}_2(\mu\text{-Cl})_2]$ (250.0 mg, 0.408 mmol) in 40 mL of acetone, 560.7 mg (1.632 mmol) of AgSbF_6 were added. The orange solution was stirred for 4 h and then was filtered to remove any insoluble material. To the filtrate, 0.816 mmol of ligand **LH** (385.6 mg of **LH1**, 410.1 mg of **LH2** or 441.1 mg of **LH3**) were added. The resulting solution was stirred for 1 h and then concentrated under reduced pressure to *ca.* 3 mL. The slow addition of Et_2O led to the precipitation of an orange solid which was washed with Et_2O (3×10 mL) and vacuum-dried to give an analytical pure compound. Yield: **1**, 820.8 mg (85 %); **2**, 865.4 mg (88 %); **3**, 828.4 mg (81 %). Crystals of **1** and **2** suitable for X-ray analysis were obtained by crystallization from CH_2Cl_2 /pentane solutions.



Compound **1**. Anal. calcd. for C₄₂H₄₃F₁₂N₂PRuSb₂: C, 42.78; H, 3.68; N, 2.37. Found: C, 42.82; H, 3.79; N, 2.41. IR (cm⁻¹): ν(SbF₆) 653 (s). HRMS (μ-TOF): C₄₂H₄₃F₁₂N₂PRuSb₂ [M-SbF₆]⁺: calc. 943.1158, found 943.1195. ¹H NMR (300.13 MHz, acetone-d₆, RT, ppm): δ = 8.97 (d, *J* = 5.5 Hz, 1H, 6-CH(Py)), 8.13-6.92 (m, 22H, H(Ar)), 7.31 (overlapped, 1H, H_{B'}), 6.77 (brd, *J* = 6.2 Hz, 1H, H_{A'}), 6.30 (dd, *J* = 6.7, 1.3 Hz, 1H, H_B), 5.66 (d, *J* = 13.4 Hz, 1H, CH₂(Ph)), 5.48 (d, *J* = 16.1 Hz, 1H, CH₂(Py)), 5.26 (m, 2H, H_A, CH₂(Ph)), 4.95 (d, *J* = 16.1 Hz, 1H, CH₂(Py)), 3.56 (dd, *J* = 13.6, 1.7 Hz, 1H, CH₂(P)), 3.36 (dd, *J* = 14.1, 4.7 Hz, 1H, CH₂(P)), 2.66 (sept, *J* = 6.9 Hz, 1H, H_I), 2.38 (s, 3H, Me), 1.13 (d, *J* = 6.9 Hz, 3H, Me_i), and 0.98 (d, *J* = 6.9 Hz, 3H, Me_i). ¹³C{¹H} NMR (75.48 MHz, acetone-d₆, RT, ppm): δ = 162.55 (s, 2-C(Py)), 157.06 (s, 6-CH(Py)), 141.40 (s, CH(Ar)), 138.01 (d, *J* = 15.2 Hz, 2-C(PhP)), 136.32 (d, *J* = 11.4 Hz, 2C, CH(Ar)), 134.99 (d, *J* = 2.3 Hz, CH(Ar)), 134.31 (d, *J* = 10.2 Hz, 2C, CH(Ar)), 134.20 (d, *J* = 9.3 Hz, CH(Ar)), 134.06 (d, *J* = 2.7 Hz, CH(Ar)), 133.19 (s, 2C, CH(Ar)), 132.46 (d, *J* = 2.3 Hz, CH(Ar)), 132.03 (s, 1-C(Ph)), 131.34 (d, *J* = 11.1 Hz, 2C, CH(Ar)), 131.15 (d, *J* = 10.9 Hz, 2C, CH(Ar)), 130.93 (d, *J* = 8.1 Hz, CH(Ar)), 130.73 (s, CH(Ar)), 130.45 (d, *J* = 2.6 Hz, CH(Ar)), 129.74 (s, 2C, CH(Ar)), 129.70 (d, *J* = 51.6 Hz, C(Ar)), 128.20 (d, *J* = 47.0 Hz, C(Ar)), 126.91 (s, CH(Ar)),

125.79 (d, $J = 52.2$ Hz, C(Ar)), 125.13 (s, CH(Ar)), 121.73 (d, $J = 5.9$ Hz, C(Cy)), 109.70 (s, C(Cy)), 97.31 (d, $J = 5.4$ Hz, C_{B'}), 92.11 (s, C_A), 89.99 (s, C_{A'}), 88.81 (s, C_B), 76.09 (s, CH₂(Ph)), 73.19 (s, CH₂(Py)), 64.29 (d, $J = 11.6$ Hz, CH₂(P)), 32.12 (s, C_{Hi}), 22.59 (s, Me_i), 21.82 (s, Me_i), and 19.65 (s, Me). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.42 MHz, acetone- d_6 , RT, ppm): $\delta = 39.83$ (s).

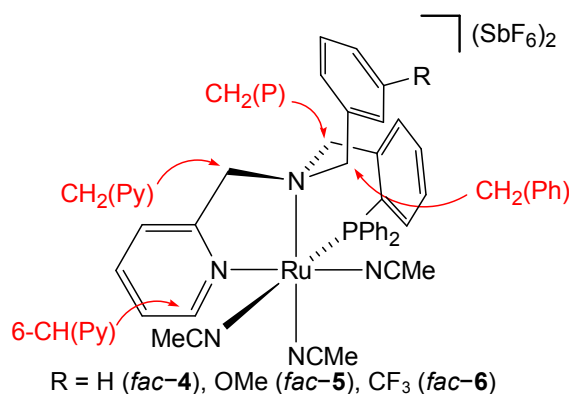
Compound **2**. Anal. calcd. for C₄₃H₄₅F₁₂N₂OPRuSb₂: C, 42.71; H, 3.75; N, 2.32. Found: C, 42.92; H, 3.46; N, 2.39. IR (cm⁻¹): $\nu(\text{SbF}_6)$ 653 (s). HRMS (μ -TOF): C₄₃H₄₅F₁₂N₂OPRuSb₂ [M-H-(SbF₆)₂]⁺: calc. 737.2241, found 737.2260. ^1H NMR (300.13 MHz, acetone- d_6 , RT, ppm): $\delta = 8.85$ (d, $J = 5.7$ Hz, 1H, 6-CH(Py)), 7.92-6.81 (m, 21H, H(Ar)), 7.25 (overlapped, 1H, H_{B'}), 6.64 (d, $J = 6.2$ Hz, 1H, H_{A'}), 6.18 (d, $J = 6.7$ Hz, 1H, H_B), 5.50 (d, $J = 13.0$ Hz, 1H, CH₂(Ph)), 5.38 (d, $J = 16.6$ Hz, 1H, CH₂(Py)), 5.12 (m, 2H, H_A, CH₂(Ph)), 4.91 (d, $J = 16.5$ Hz, 1H, CH₂(Py)), 3.67 (s, 3H, OMe), 3.41 (brd, $J = 13.8$ Hz, 1H, CH₂(P)), 3.23 (dd, $J = 13.9, 4.6$ Hz, 1H, CH₂(P)), 2.53 (sept, $J = 6.9$ Hz, 1H, H_i), 2.25 (s, 3H, Me), 1.00 (d, $J = 6.9$ Hz, 3H, Me_i), and 0.84 (d, $J = 6.9$ Hz, 3H, Me_r). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.48 MHz, acetone- d_6 , RT, ppm): $\delta = 162.11$ (s, 2-C(Py)), 160.52 (s, C(OMe)), 156.78 (d, $J = 1.6$ Hz, 6-CH(Py)), 141.09 (s, CH(Ar)), 137.86 (d, $J = 13.3$ Hz, 2-C(PhP)), 136.06 (d, $J = 11.9$ Hz, 2C, CH(Ar)), 134.17 (d, $J = 2.7$ Hz, CH(Ar)), 134.02 (d, $J = 10.2$ Hz, 2C, CH(Ar)), 133.93 (d, $J = 9.6$ Hz, CH(Ar)), 133.75 (d, $J = 2.5$ Hz, CH(Ar)), 133.18 (s, 1-C(Ph)), 132.13 (d, $J = 2.5$ Hz, CH(Ar)), 131.05 (d, $J = 11.1$ Hz, 2C, CH(Ar)), 130.86 (d, $J = 10.9$ Hz, 2C, CH(Ar)), 130.58 (d, $J = 8.1$ Hz, CH(Ar)), 130.53 (s, CH(Ar)), 130.13 (d, $J = 2.9$ Hz, CH(Ar)), 130.04 (d, $J = 55.5$ Hz, C(Ar)), 127.90 (d, $J = 47.0$ Hz, C(Ar)), 126.60 (s, CH(Ar)), 125.48 (d, $J = 54.0$ Hz, C(Ar)), 124.85 (s, 2C, CH(Ar)), 121.34 (d, $J = 4.5$ Hz, C(Cy)), 118.61 (s, CH(Ar)), 115.45 (s, CH(Ar)), 109.33 (s, C(Cy)), 97.02 (d, $J = 4.6$ Hz, C_{B'}), 91.73 (s, C_A), 89.66 (s, C_{A'}), 88.49 (s, C_B), 75.66 (s, CH₂(Ph)), 73.12 (s,

CH₂(Py)), 64.03 (d, $J = 11.4$ Hz, CH₂(P)), 55.43 (s, OMe), 31.79 (s, C_{Hi}), 22.31 (s, Me_i), 21.47 (s, Me_i), and 19.45 (s, Me). $^3\text{P}\{^1\text{H}\}$ NMR (121.42 MHz, acetone-*d*₆, RT, ppm): $\delta = 39.82$ (s).

Compound **3**. Anal. calcd. for C₄₃H₄₂F₁₅N₂PRuSb₂: C, 41.41; H, 3.39; N, 2.25. Found: C, 41.68; H, 3.58; N, 2.42. IR (cm⁻¹): $\nu(\text{SbF}_6)$ 653 (s). HRMS (μ -TOF): C₄₃H₄₂F₁₅N₂PRuSb₂ [M-H-(SbF₆)₂]⁺: calc. 775.2009, found 775.1999. ^1H NMR (400.16 MHz, acetone-*d*₆, RT, ppm): $\delta = 8.96$ (d, $J = 5.7$ Hz, 1H, 6-CH(Py)), 8.06-6.96 (m, 21H, H(Ar)), 7.30 (dd, $J = 6.2, 1.0$ Hz, 1H, H_{B'}), 6.75 (dd, $J = 6.3, 1.0$ Hz, 1H, H_{A'}), 6.29 (dd, $J = 6.0, 1.1$ Hz, 1H, H_B), 5.81 (d, $J = 13.5$ Hz, 1H, CH₂(Ph)), 5.60 (brd, $J = 15.6$ Hz, 1H, CH₂(Py)), 5.42 (d, $J = 13.5$ Hz, 1H, CH₂(Ph)), 5.29 (ddd, $J = 6.7, 3.1, 1.2$ Hz, 1H, H_A), 5.06 (d, $J = 15.8$ Hz, 1H, CH₂(Py)), 3.65 (dd, $J = 13.7, 1.8$ Hz, 1H, CH₂(P)), 3.46 (dd, $J = 13.7, 4.7$ Hz, 1H, CH₂(P)), 2.67 (sept, $J = 7.0$ Hz, 1H, H_i), 2.39 (s, 3H, Me), 1.13 (d, $J = 7.0$ Hz, 3H, Me_i), and 0.99 (d, $J = 7.0$ Hz, 3H, Me_i). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.62 MHz, acetone-*d*₆, RT, ppm): $\delta = 162.40$ (s, 2-C(Py)), 157.02 (s, 6-CH(Py)), 141.44 (s, CH(Ar)), 137.94 (d, $J = 15.3$ Hz, 2-C(PhP)), 137.21 (d, $J = 2.7$ Hz, CH(Ar)), 136.31 (d, $J = 11.3$ Hz, 2C, CH(Ar)), 134.45 (d, $J = 2.3$ Hz, CH(Ar)), 134.28 (d, $J = 10.2$ Hz, 2C, CH(Ar)), 134.27 (d, $J = 9.4$ Hz, CH(Ar)), 134.02 (d, $J = 2.8$ Hz, CH(Ar)), 133.26 (s, 1-C(Ph)), 132.44 (d, $J = 2.0$ Hz, CH(Ar)), 131.47 (d, $J = 11.1$ Hz, 2C, CH(Ar)), 131.37 (q, $J = 32.6$ Hz, C(CF₃)), 131.17 (d, $J = 10.8$ Hz, 2C, CH(Ar)), 130.97 (d, $J = 8.1$ Hz, CH(Ar)), 130.85 (s, CH(Ar)), 130.44 (d, $J = 2.6$ Hz, CH(Ar)), 130.31 (d, $J = 55.9$ Hz, C(Ar)), 129.66 (q, $J = 3.8$ Hz, CH(Ar)), 128.14 (d, $J = 47.1$ Hz, C(Ar)), 127.50 (q, $J = 3.8$ Hz, CH(Ar)), 126.98 (s, CH(Ar)), 125.75 (d, $J = 54.0$ Hz, C(Ar)), 125.13 (s, CH(Ar)), 124.98 (q, $J = 271.5$ Hz, CF₃), 121.91 (d, $J = 6.0$ Hz, C(Cy)), 109.66 (s, C(Cy)), 97.02 (d, $J = 5.5$ Hz, C_{B'}), 92.18 (s, C_A), 90.11 (s, C_{A'}), 88.57 (s, C_B), 75.06 (s, CH₂(Ph)), 73.10 (s, CH₂(Py)), 64.26 (d, $J = 11.2$ Hz, CH₂(P)),

32.09 (s, C_{Hi}), 22.52 (s, Me_i), 21.80 (s, Me_i), and 19.65 (s, Me). $^{19}\text{F}\{^1\text{H}\}$ NMR (282.33 MHz, acetone-*d*₆, RT, ppm): $\delta = -62.90$ (s). $^{31}\text{P}\{^1\text{H}\}$ NMR (161.98 MHz, acetone-*d*₆, RT, ppm): $\delta = 39.52$ (s).

Preparation and characterization of the complex *fac*-[Ru($\kappa^3\text{N},\text{N}',\text{P}$ -LH)(NCMe)₃][SbF₆]₂ (LH = LH1 (*fac*-4), LH2 (*fac*-5), LH3 (*fac*-6)). A solution of the complex [(Cy)Ru($\kappa^3\text{N},\text{N}',\text{P}$ -LH)][SbF₆]₂ (250.0 mg, 0.209 mmol of **1**, 0.207 mmol of **2** or 0.198 mmol of **3**) in 20 mL of MeCN was heated at 65 °C for 48 h. The resulting solution was concentrated under reduced pressure to *ca.* 1 mL. The slow addition of a 70/30 mixture Et₂O/pentane led to the precipitation of an orange-brown solid. The solid was washed with Et₂O (5 × 10 mL) and vacuum-dried to give an analytical pure compound. Yield: *fac*-4, 161.8 mg (65 %); *fac*-5, 166.7 mg (67 %); *fac*-6, 200.6 mg (81 %).



Compound *fac*-4. Anal. Calcd. for C₃₈H₃₈F₁₂N₅PRuSb₂: C, 39.07; H, 3.28; N, 5.99. Found: C, 38.86; H, 3.17; N, 5.79. HRMS (μ -TOF): C₃₈H₃₈F₁₂N₅PRuSb₂ [M-NCMe-SbF₆]⁺: calc. 891.0591, found 891.0619. ^1H NMR (400.16 MHz, CD₂Cl₂, RT, ppm): $\delta = 8.49$ (d, *J* = 5.6 Hz, 1H, 6-CH(Py)), 7.82-6.85 (m, 22H, H_{Ar}), 4.66 (d, *J* = 15.6 Hz, 1H, CH₂(Py)), 4.40 (d, *J* = 13.9 Hz, 1H, CH₂(Ph)), 4.02 (dd, *J* = 14.0, 2.3 Hz, 1H, CH₂(P)), 4.01 (d, *J* = 13.9 Hz, 1H, CH₂(Ph)), 3.68 (d, *J* = 15.6 Hz, 1H, CH₂(Py)), 3.56 (d, *J* = 13.9 Hz, 1H, CH₂(P)), 2.55 (s, 3H, CNMe), 2.45 (s, 3H, CNMe), and 2.42 (s, 3H, CNMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.62 MHz, CD₂Cl₂, RT, ppm): $\delta = 159.51$ (s, 2-

C(Py)), 154.08 (s, 6-CH(Py)), 137.98 (s, CH(Ar)), 137.90 (d, $J = 16.2$ Hz, 2-C(PhP)), 134.69 (d, $J = 9.8$ Hz, 2C, CH(Ar)), 133.66 (d, $J = 9.0$ Hz, CH(Ar)), 132.51 (s, 2C, CH(Ar)), 132.43 (d, $J = 9.8$ Hz, 2C, CH(Ar)), 132.15 (brs, 2C, CH(Ar)), 131.94 (brs, CH(Ar)), 130.90 (brs, CH(Ar)), 130.41 (d, $J = 7.3$ Hz, CH(Ar)), 129.85 (s, 1-C(Ph)), 129.72 (brs, CH(Ar)), 129.12 (d, $J = 9.8$ Hz, 2C, CH(Ar)), 129.08 (s, CH(Ar)), 129.01 (d, $J = 11.1$ Hz, 2C, CH(Ar)), 128.86 (s, CH(Ar)), 128.33 (s, MeCN), 128.25 (d, $J = 45.4$ Hz, C(Ar)), 127.85 (s, MeCN), 127.76 (d, $J = 52.4$ Hz, C(Ar)), 126.27 (d, $J = 49.3$ Hz, C(Ar)), 125.21 (d, $J = 14.6$ Hz, MeCN), 124.78 (s, CH(Ar)), 122.20 (s, CH(Ar)), 65.48 (s, CH₂(Py)), 65.01 (s, CH₂(Ph)), 61.94 (d, $J = 8.1$ Hz, CH₂(P)), 4.03 (s, CNMe), 3.80 (s, CNMe), and 3.56 (s, CNMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (161.98 MHz, CD₂Cl₂, RT, ppm): $\delta = 52.19$ (s).

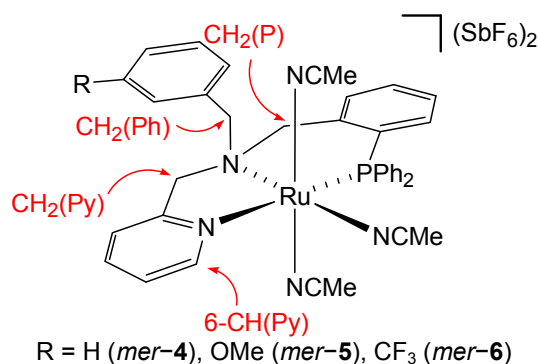
Compound *fac*-**5**. Anal. Calcd. for C₃₉H₄₀F₁₂N₅OPRuSb₂: C, 39.09; H, 3.36; N, 5.84 Found: C, 39.25; H, 3.38; N 5.66. HRMS (μ -TOF): C₃₉H₄₀F₁₂N₅OPRuSb₂ [M–NCMe–SbF₆]⁺: calc. 921.0697, found 921.0697. ^1H NMR (300.13 MHz, CD₂Cl₂, RT, ppm): $\delta = 8.45$ (d, $J = 5.3$ Hz, 1H, 6-CH(Py)), 7.67–6.85 (m, 21H, H_{Ar}), 4.58 (d, $J = 15.5$ Hz, 1H, CH₂(Py)), 4.32 (d, $J = 13.8$ Hz, 1H, CH₂(Ph)), 4.03 (dd, $J = 13.9, 2.3$ Hz, 1H, CH₂(P)), 3.95 (d, $J = 13.8$ Hz, 1H, CH₂(Ph)), 3.89 (s, 3H, OMe), 3.67 (d, $J = 15.5$ Hz, 1H, CH₂(Py)), 3.56 (d, $J = 13.9$ Hz, 1H, CH₂(P)), 2.52 (s, 3H, CNMe), 2.42 (s, 3H, CNMe), and 2.37 (s, 3H, CNMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.48 MHz, CD₂Cl₂, RT, ppm): $\delta = 160.88$ (s, C(OMe)), 160.33 (s, 2-C(Py)), 154.87 (s, 6-CH(Py)), 138.01 (s, CH(Ar)), 137.95 (d, $J = 14.8$ Hz, 2-C(PhP)), 134.58 (d, $J = 10.2$ Hz, 2C, CH(Ar)), 133.54 (d, $J = 9.1$ Hz, CH(Ar)), 132.40 (d, $J = 9.4$ Hz, 2C, CH(Ar)), 132.26 (brs, CH(Ar)), 132.07 (brs, CH(Ar)), 131.93 (brs, CH(Ar)), 131.17 (s, 1-C(Ph)), 130.89 (brs, CH(Ar)), 130.35 (d, $J = 7.4$ Hz, CH(Ar)), 130.14 (s, CH(Ar)), 129.10 (d, $J = 10.2$ Hz, 2C, CH(Ar)), 128.88 (d, $J = 10.0$ Hz, 2C, CH(Ar)), 128.30 (s, MeCN), 128.06 (d, $J = 45.6$ Hz,

C(Ar)), 127.82 (d, $J = 52.9$ Hz, C(Ar)), 127.79 (s, MeCN), 126.23 (d, $J = 48.8$ Hz, C(Ar)), 125.14 (d, $J = 14.0$ Hz, MeCN), 124.79 (s, CH(Ar)), 124.55 (s, CH(Ar)), 122.16 (s, CH(Ar)), 118.35 (s, CH(Ar)), 114.78 (s, CH(Ar)), 66.26 (s, CH₂(Py)), 62.83 (d, $J = 7.6$ Hz, CH₂(P)), 66.00 (s, CH₂(Ph)), 56.27 (s, OMe), 4.90 (s, CNMe), 4.66 (s, CNMe), and 4.43 (s, CNMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.42 MHz, CD₂Cl₂, RT, ppm): $\delta = 52.11$ (s).

Compound *fac*-6. Anal. Calcd. for C₃₉H₃₇F₁₅N₅PRuSb₂: C, 37.89; H, 3.02; N, 5.66. Found: C, 38.13; H, 3.16; N, 5.80. HRMS (μ -TOF): C₃₉H₃₇F₁₅N₅PRuSb₂ [M–NCMe–SbF₆]⁺: calc. 959.0465, found 959.0423. ^1H NMR (400.16 MHz, CD₂Cl₂, RT, ppm): $\delta = 8.40$ (d, $J = 5.6$ Hz, 1H, 6-CH(Py)), 7.87–6.69 (m, 21H, H_{Ar}), 4.63 (d, $J = 15.4$ Hz, 1H, CH₂(Py)), 4.43 (d, $J = 14.0$ Hz, 1H, CH₂(Ph)), 3.98 (d, $J = 14.0$ Hz, 1H, CH₂(Ph)), 3.85 (brd, $J = 13.4$ Hz, 1H, CH₂(P)), 3.69 (d, $J = 15.4$ Hz, 1H, CH₂(Py)), 3.46 (brd, $J = 13.6$ Hz, 1H, CH₂(P)), 2.47 (s, 3H, CNMe), 2.40 (s, 3H, CNMe), and 2.35 (s, 3H, CNMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.62 MHz, CD₂Cl₂, RT, ppm): $\delta = 159.18$ (s, 2-C(Py)), 154.12 (s, 6-CH(Py)), 138.04 (s, CH(Ar)), 137.42 (d, $J = 15.2$ Hz, 2-C(PhP)), 136.15 (s, CH(Ar)), 134.75 (d, $J = 9.5$ Hz, 2C, CH(Ar)), 133.55 (d, $J = 9.1$ Hz, CH(Ar)), 132.35 (d, $J = 9.9$ Hz, 2C, CH(Ar)), 132.18 (brs, 2C, CH(Ar)), 132.02 (brs, CH(Ar)), 130.92 (s, CH(Ar)), 133.87 (s, 1-C(Ph)), 130.66 (q, $J = 44.0$ Hz, C(CF₃)), 130.70 (s, CH(Ar)), 129.36 (brs, CH(Ar)), 129.14 (d, $J = 10.2$ Hz, 2C, CH(Ar)), 129.06 (brs, CH(Ar)), 128.93 (d, $J = 10.2$ Hz, 2C, CH(Ar)), 128.25 (d, $J = 46.3$ Hz, C(Ar)), 127.98 (s, MeCN), 127.82 (s, MeCN), 127.55 (d, $J = 53.5$ Hz, C(Ar)), 126.50 (brs, CH(Ar)), 126.21 (d, $J = 48.5$ Hz, C(Ar)), 125.45 (d, $J = 14.7$ Hz, MeCN), 124.82 (s, CH(Ar)), 123.95 (q, $J = 272.7$ Hz, CF₃), 122.32 (s, CH(Ar)), 65.70 (s, CH₂(Py)), 64.33 (s, CH₂(Ph)), 61.99 (d, $J = 8.1$ Hz, CH₂(P)), 4.05 (s, CNMe), 3.80 (s, CNMe), and 3.52 (s,

CNMe). $^{19}\text{F}\{^1\text{H}\}$ NMR (282.33 MHz, CD_2Cl_2 , RT, ppm): $\delta = -62.86$ (s). $^{31}\text{P}\{^1\text{H}\}$ NMR (161.98 MHz, CD_2Cl_2 , RT, ppm): $\delta = 52.04$ (s).

Preparation and characterization of the complex $\text{mer-}[\text{Ru}(\kappa^3\text{N},\text{N}',\text{P-LH})(\text{NCMe})_3][\text{SbF}_6]_2$ (LH = LH1 (*mer-4*), LH2 (*mer-5*), LH3 (*mer-6*)). A solution of the complex $\text{fac-}[\text{Ru}(\kappa^3\text{N},\text{N}',\text{P-LH})(\text{NCMe})_3][\text{SbF}_6]_2$ (200.0 mg, 0.169 mmol of *fac-4*, 0.167 mmol of *fac-5* or 0.160 mmol of *fac-6*) in 20 mL of MeOH was refluxed for 48 h. The resulting solution was concentrated under reduced pressure to *ca.* 1 mL. The slow addition of a 70/30 mixture Et_2O /pentane led to the precipitation of an orange-brown solid. The solid was washed with Et_2O (2×10 mL) and vacuum-dried to give analytical and spectroscopically pure compounds *mer-4* and *mer-5*. A 60/40, *fac-6*/*mer-6* molar ratio mixture was recovered for complex **6**. Yield: *mer-4*, 170.4 mg (85 %); *mer-5*, 176.2 mg (88 %) Crystals of *mer-5* suitable for X-ray analysis were obtained by crystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ solutions.



Compound *mer-4*. Anal. Calcd. for $\text{C}_{38}\text{H}_{38}\text{F}_{12}\text{N}_5\text{PRuSb}_2$: C, 39.07; H, 3.28; N, 5.99. Found: C, 39.27; H, 3.44; N, 5.89. HRMS (μ -TOF): $\text{C}_{38}\text{H}_{38}\text{F}_{12}\text{N}_5\text{PRuSb}_2$ $[\text{M}-\text{NCMe}-\text{SbF}_6]^+$: calc. 891.0591, found 891.0592. ^1H NMR (500.13 MHz, CD_2Cl_2 , RT, ppm): $\delta = 9.14$ (m, 1H, 6-CH(Py)), 8.22-7.01 (m, 22H, H_{Ar}), 4.45 (d, $J = 16.3$ Hz, 1H, $\text{CH}_2(\text{Py})$), 4.19 (d, $J = 16.3$ Hz, 1H, $\text{CH}_2(\text{Py})$), 4.06 (d, $J = 14.2$ Hz, 1H, $\text{CH}_2(\text{P})$), 3.95 (dd, $J = 14.2, 2.2$ Hz, 1H, $\text{CH}_2(\text{P})$), 3.71 (d, $J = 13.9$ Hz, 1H, $\text{CH}_2(\text{Ph})$), 3.44 (d, $J =$

13.9 Hz, 1H, CH₂(Ph)), 2.55 (s, 3H, CNMe), 2.22 (s, 3H, CNMe), and 1.81 (s, 3H, CNMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.77 MHz, CD₂Cl₂, RT, ppm): δ = 157.35 (s, 2-C(Py)), 152.14 (s, 6-CH(Py)), 139.85 (s, CH(Ar)), 139.92 (d, J = 17.8 Hz, 2-C(PhP)), 136.63 (brs, CH(Ar)), 135.20 (d, J = 9.7 Hz, CH(Ar)), 132.91 (d, J = 10.0 Hz, 2C, CH(Ar)), 132.63 (d, J = 9.7 Hz, 2C, CH(Ar)), 132.62 (d, J = 2.1 Hz, CH(Ar)), 132.24 (s, 2C, CH(Ar)), 131.30 (d, J = 2.4 Hz, CH(Ar)), 131.05 (d, J = 2.4 Hz, CH(Ar)), 130.44 (d, J = 7.0 Hz, CH(Ar)), 129.89 (s, CH(Ar)), 129.73 (d, J = 48.4 Hz, C(Ar)), 129.41 (d, J = 46.0 Hz, C(Ar)), 129.30 (d, J = 9.8 Hz, 2C, CH(Ar)), 129.22 (s, 1-C(Ph)), 128.95 (s, 2C, CH(Ar)), 128.84 (d, J = 10.0 Hz, 2C, CH(Ar)), 127.83 (s, MeCN), 127.59 (s, MeCN), 126.51 (s, MeCN), 126.26 (d, J = 2.2 Hz, CH(Ar)), 125.64 (d, J = 45.9 Hz, C(Ar)), 123.700 (d, J = 2.1 Hz, CH(Ar)), 64.41 (s, CH₂(Py)), 63.04 (d, J = 6.2 Hz, CH₂(P)), 61.27 (s, CH₂(Ph)), 4.21 (s, CNMe), 3.93 (s, CNMe), and 3.42 (s, CNMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.46 MHz, CD₂Cl₂, RT, ppm): δ = 50.80 (s).

Compound *mer*-**5**. Anal. Calcd. for C₃₉H₄₀F₁₂N₅OPRuSb₂: C, 39.09; H, 3.36; N, 5.84 Found: C, 39.23; H, 3.44; N 5.89. HRMS (μ -TOF): C₃₉H₄₀F₁₂N₅OPRuSb₂ [M-SbF₆]⁺: calc. 962.0963, found 962.0925. ^1H NMR (300.13 MHz, CD₂Cl₂, RT, ppm): δ = 9.12 (m, 1H, 6-CH(Py)), 8.19-6.55 (m, 21H, H_{Ar}), 4.49 (d, J = 16.1 Hz, 1H, CH₂(Py)), 4.19 (d, J = 16.1 Hz, 1H, CH₂(Py)), 4.07 (d, J = 14.0 Hz, 1H, CH₂(P)), 3.98 (dd, J = 14.0, 2.3 Hz, 1H, CH₂(P)), 3.83 (s, 3H, OMe), 3.68 (d, J = 13.9 Hz, 1H, CH₂(Ph)), 3.41 (d, J = 13.9 Hz, 1H, CH₂(Ph)), 2.54 (s, 3H, CNMe), 2.21 (s, 3H, CNMe), and 1.81 (s, 3H, CNMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.48 MHz, CD₂Cl₂, RT, ppm): δ = 160.88 (s, C(OMe)), 160.33 (s, 2-C(Py)), 154.87 (s, 6-CH(Py)), 139.94 (d, J = 16.8 Hz, 2-C(PhP)), 139.87 (s, CH(Ar)), 135.22 (d, J = 9.8 Hz, CH(Ar)), 134.68 (s, CH(Ar)), 132.84 (d, J = 9.9 Hz, 2C, CH(Ar)), 132.62 (d, J = 9.8 Hz, 2C, CH(Ar)), 132.49 (brs, CH(Ar)), 131.23 (brs, CH(Ar)), 131.02 (brs, CH(Ar)), 130.56 (s, 1-C(Ph)), 130.45 (d, J

= 6.7 Hz, CH(Ar)), 130.04 (d, $J = 38.0$ Hz, C(Ar)), 129.95 (s, CH(Ar)), 129.29 (d, $J = 46.4$ Hz, C(Ar)), 129.28 (d, $J = 10.1$ Hz, 2C, CH(Ar)), 128.81 (d, $J = 9.8$ Hz, 2C, CH(Ar)), 128.30 (s, MeCN), 127.41 (s, MeCN), 126.22 (s, CH(Ar)), 125.63 (d, $J = 46.3$ Hz, C(Ar)), 126.08 (s, MeCN), 124.21 (s, CH(Ar)), 123.62 (s, CH(Ar)), 118.10 (s, CH(Ar)), 115.04 (s, CH(Ar)), 66.00 (s, CH₂(Ph)), 66.26 (s, CH₂(Py)), 62.83 (d, $J = 7.6$ Hz, CH₂(P)), 56.27 (s, OMe), 4.90 (s, CNMe), 4.66 (s, CNMe), and 4.43 (s, CNMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.42 MHz, CD₂Cl₂, RT, ppm): $\delta = 50.80$ (s).

Compound *mer*-**6** (characterized in a *mer*-**6**/*fac*-**6**, 40/60 molar ratio mixture). ^1H NMR (500.13 MHz, CD₂Cl₂, RT, ppm): $\delta = 9.19$ (m, 1H, 6-CH(Py)), 8.26-6.78 (m, 21H, H_{Ar}), 4.44 (d, $J = 16.3$ Hz, 1H, CH₂(Py)), 4.33 (d, $J = 16.3$ Hz, 1H, CH₂(Py)), 4.15 (d, $J = 14.1$ Hz, 1H, CH₂(P)), 3.93 (m, 1H, CH₂(P)), 3.84 (d, $J = 14.0$ Hz, 1H, CH₂(Ph)), 3.55 (d, $J = 10.0$ Hz, 1H, CH₂(Ph)), 2.60 (s, 3H, CNMe), 2.27 (s, 3H, CNMe), and 1.87 (s, 3H, CNMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.77 MHz, CD₂Cl₂, RT, ppm): $\delta = 156.96$ (s, 2-C(Py)), 152.28 (s, 6-CH(Py)), 140.05 (s, CH(Ar)), 139.52 (d, $J = 17.7$ Hz, 2-C(PhP)), 135.7-121.5 (m, 26C, Ar, CF₃), 128.08 (s, MeCN), 127.74 (s, MeCN), 126.68 (s, MeCN), 64.48 (s, CH₂(Py)), 63.18 (d, $J = 6.1$ Hz, CH₂(P)), 60.52 (s, CH₂(Ph)), 4.15 (s, CNMe), 3.86 (s, CNMe), and 3.39 (s, CNMe). $^{19}\text{F}\{^1\text{H}\}$ NMR (282.33 MHz, CD₂Cl₂, RT, ppm): $\delta = -62.74$ (s). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.46 MHz, CD₂Cl₂, RT, ppm): $\delta = 50.73$ (s).

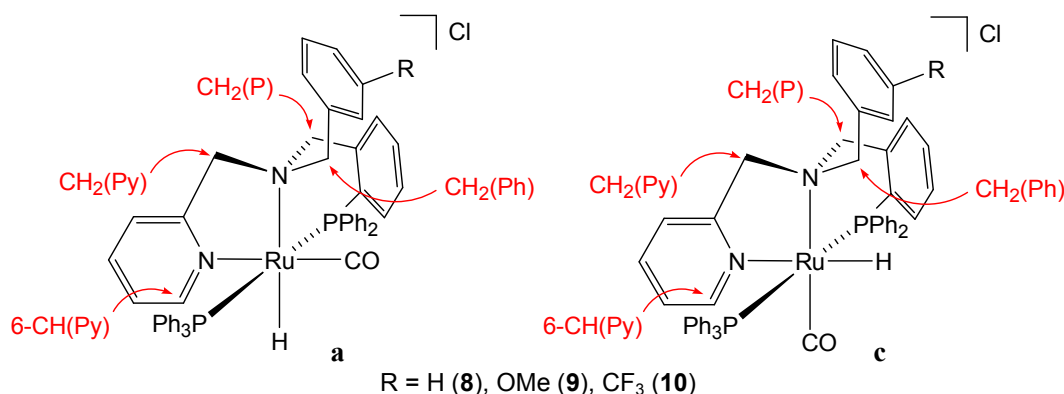
Preparation and characterization of the complex [RuCl₂(PPh₃)($\kappa^3\text{N},\text{N}',\text{P}$ -LH1)]

(**7**). To a suspension of [RuCl₂(PPh₃)₃] (202.5 mg, 0.212 mmol) in 20 mL of *tert*-butanol, 100.0 mg (0.212 mmol) of **LH1** were added. The resulting suspension was stirred under reflux for 4 hours. After the reaction time, the red solution was vacuum-dried and the residue was recrystallized from MeOH/CH₂Cl₂/Et₂O solution, washed with Et₂O (4 × 10 mL) and vacuum-dried to give an analytical pure compound. Yield: 185.7 mg (97 %). Anal. Calcd for C₅₀H₄₄Cl₂N₂P₂Ru·CH₂Cl₂: C, 61.77; H, 4.67; N, 2.82.

Chemical structure of a ruthenium complex (7). The central ruthenium atom (Ru) is coordinated by two chlorine atoms (Cl), two phosphine ligands (PPh₂ and PPh₃), and a bidentate ligand. The bidentate ligand consists of a central nitrogen atom (N) bonded to two phenyl rings. The left phenyl ring is substituted with a CH₂(Ph) group and a CH₂(Py) group. The right phenyl ring is substituted with a CH₂(P) group and a 6-CH(Py) group. The ruthenium atom is also coordinated to a CH₂(P) group and a 6-CH(Py) group.

suspension of $[\text{RuClH}(\text{CO})(\text{PPh}_3)_3]$ (1.500 g, 1.57 mmol) in 40 mL of EtOH, 1.57 mmol of **LH** (744.2 mg of **LH1**, 791.5 mg of **LH2** or 851.3 mg of **LH3**) were added. The resulting suspension was stirred under reflux for 48 hours. After the reaction time, the solution was vacuum-dried and the residue was firstly recrystallized from MeOH/ CH_2Cl_2 /Et₂O solution, washed with Et₂O (4 × 10 mL) and finally vacuum-dried to give an analytical pure compound. Yield: **8**, 1.123 g (79 %); **9**, 1.195 g (82 %); **10**,

1.306 g (86 %). Crystals of **10** suitable for X-ray analysis were obtained by crystallization from EtOH/Et₂O/pentane solutions.



Compound **8**. Anal. Calcd for C₅₁H₄₅ClN₂OP₂Ru·CH₂Cl₂: C, 63.39; H, 4.81; N, 2.84. Found: C, 63.49; H, 4.74; N, 3.01. IR (cm⁻¹): ν(CO) 924 (s). HRMS (μ-TOF): C₅₁H₄₅ClN₂OP₂Ru [M-Cl]⁺: calc. 865.2059, found 865.2086. The isolated solid was characterized by NMR as a mixture of isomers: at 298 K, in *ca.* 98:2 (**8a**/**8c**) and at 313 K, in *ca.* 75/23/2 (**8a**/**8a'**/**8c**) molar ratio.

8a (98 %). ¹H NMR (300.13 MHz, CD₃OD, RT, ppm): δ = 8.30-6.35 (38H, H(Ar)), 4.36 (brd, *J* = 13.8 Hz, 1H, CH₂(Py)), 4.33 (brd, *J* = 14.4 Hz, 1H, CH₂(Py)), 4.04 (brd, *J* = 14.4 Hz, 1H, CH₂(Ph)), 3.99 (br, 1H, CH₂(P)), 3.77 (brd, *J* = 15.0 Hz, 1H, CH₂(Ph)), 3.57 (brd, *J* = 12.4 Hz, 1H, CH₂(P)), and -13.33 (pt, *J* = 22.7 Hz, RuH). ¹³C{¹H} NMR (75.48 MHz, CD₃OD, RT, ppm): δ = 204.99 (br, CO), 158.08 (brs, 2-C(Py)), 154.77 (brs, 6-CH(Py)), 139.00-121.16 (46C, Ar), 65.61 (brs, 2C, CH₂(Py), CH₂(P)), and 60.73 (br, CH₂(Ph)). ³¹P{¹H} NMR (121.42 MHz, CD₃OD, 298 K, ppm): δ = 41.88 (AB system, *J* = 255.9 Hz, PPh₃) and 40.57 (AB system, *J* = 255.9 Hz, PPh₂).

8a (75 %). ¹H NMR (500.13 MHz, CD₃OD, 213 K, ppm): δ = -13.17 (pt, *J* = 23.3 Hz, RuH). ³¹P{¹H} NMR (202.46 MHz, CD₃OD, 213, ppm): δ = 41.62 (AB system, *J* = 253.5 Hz, PPh₃) and 40.84 (AB system, *J* = 253.5 Hz, PPh₂).

8a' (23 %). ^1H NMR (500.13 MHz, CD_3OD , 213 K, ppm): $\delta = -12.82$ (dd, $J = 28.2, 15.6$ Hz, RuH). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.46 MHz, CD_3OD , 213, ppm): $\delta = 43.96$ (AB system, $J = 253.8$ Hz, PPh_3) and 40.12 (AB system, $J = 253.8$ Hz, PPh_2).

8c (2 %). ^1H NMR (300.13 MHz, CD_3OD , RT, ppm): $\delta = -11.28$ (dd, $J = 23.7, 18.7$ Hz, RuH). ^1H NMR (500.13 MHz, CD_3OD , 213 K, ppm): $\delta = -11.01$ (dd, $J = 23.3, 18.5$ Hz, RuH). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.46 MHz, CD_3OD , 213, ppm): $\delta = 43.58$ (d, $J = 256.1$ Hz, PPh_3) and 36.78 (d, $J = 256.1$ Hz, PPh_2).

Compound **9**. Anal. Calcd for $\text{C}_{52}\text{H}_{47}\text{ClN}_2\text{O}_2\text{P}_2\text{Ru}\cdot\text{CH}_2\text{Cl}_2$: C, 62.70; H, 4.86; N, 2.76. Found: C, 62.49; H, 4.95; N, 2.68. IR (cm^{-1}): $\nu(\text{CO})$ 1925 (s). HRMS (μ -TOF): $\text{C}_{52}\text{H}_{47}\text{ClN}_2\text{O}_2\text{P}_2\text{Ru} [\text{M}-\text{Cl}]^+$: calc. 895.2165, found 895.2113. The isolated solid was characterized by NMR as a mixture of isomers: at 298 K, in *ca.* 97:3 (**9a**/**9c**) and at 313 K, in *ca.* 71/26/3 (**9a**/**9a'**/**9c**) molar ratio.

9a (97 %). ^1H NMR (300.13 MHz, CD_3OD , RT, ppm): $\delta = 8.00$ -6.21 (37H, H(Ar)), 4.33 (brd, $J = 13.7$ Hz, 1H, $\text{CH}_2(\text{Py})$), 4.30 (brd, $J = 14.9$ Hz, 1H, $\text{CH}_2(\text{Py})$), 4.00 (brd, $J = 14.1$ Hz, 2H, $\text{CH}_2(\text{Ph})$, $\text{CH}_2(\text{P})$), 3.83 (s, 3H, OMe), 3.81 (brd, $J = 15.5$ Hz, 1H, $\text{CH}_2(\text{Ph})$), 3.58 (br, 1H, $\text{CH}_2(\text{P})$), and -13.34 (pt, $J = 22.7$ Hz, RuH). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.48 MHz, CD_3OD , RT, ppm): $\delta = 205.00$ (pt, $J = 16.6$ Hz, CO), 159.77 (s, C(OMe)), 158.06 (br, 2-C(Py)), 154.67 (br, 6-CH(Py)), 138.72-113.60 (45C, Ar), 65.66 (brs, 2C, $\text{CH}_2(\text{Py})$, $\text{CH}_2(\text{P})$), 58.63 (br, $\text{CH}_2(\text{Ph})$), and 54.56 (s, OMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.42 MHz, CD_3OD , 298 K, ppm): $\delta = 41.82$ (AB system, $J = 255.1$ Hz, PPh_3) and 40.58 (AB system, $J = 255.1$ Hz, PPh_2).

9a (71 %). ^1H NMR (500.13 MHz, CD_3OD , 213 K, ppm): $\delta = -13.19$ (pt, $J = 23.3$ Hz, RuH). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.46 MHz, CD_3OD , 213, ppm): $\delta = 41.58$ (AB system, $J = 254.3$ Hz, PPh_3) and 40.84 (AB system, $J = 254.3$ Hz, PPh_2).

9a' (26 %). ^1H NMR (500.13 MHz, CD_3OD , 213 K, ppm): $\delta = -12.83$ (dd, $J = 28.6, 15.7$ Hz, RuH). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.46 MHz, CD_3OD , 213, ppm): $\delta = 43.91$ (AB system, $J = 253.5$ Hz, PPh_3) and 40.25 (AB system, $J = 253.5$ Hz, PPh_2).

9c (3 %). ^1H NMR (300.13 MHz, CD_3OD , RT, ppm): $\delta = -11.29$ (dd, $J = 23.7, 18.8$ Hz, RuH). ^1H NMR (500.13 MHz, CD_3OD , 213 K, ppm): $\delta = -11.01$ (dd, $J = 23.8, 19.7$ Hz, RuH). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.46 MHz, CD_3OD , 213, ppm): $\delta = 43.51$ (d, $J = 256.3$ Hz, PPh_3) and 36.75 (d, $J = 256.3$ Hz, PPh_2).

Compound **10**. Anal. Calcd for $\text{C}_{52}\text{H}_{44}\text{F}_3\text{ClN}_2\text{OP}_2\text{Ru}\cdot\text{OH}_2$: C, 63.32; H, 4.70; N, 2.84. Found: C, 63.16; H, 4.91; N, 2.52. IR (cm^{-1}): $\nu(\text{CO})$ 929 (s). HRMS (μ -TOF): $\text{C}_{52}\text{H}_{44}\text{F}_3\text{ClN}_2\text{OP}_2\text{Ru} [\text{M}-\text{HPPH}_3]^+$: calc. 705.0624, found 705.0634. The isolated solid was characterized by NMR as a mixture of isomers: at 298 K, in *ca.* 98:2 (**10a**/**10c**) and at 313 K, in *ca.* 73/25/2 (**10a**/**10a'**/**10c**) molar ratio.

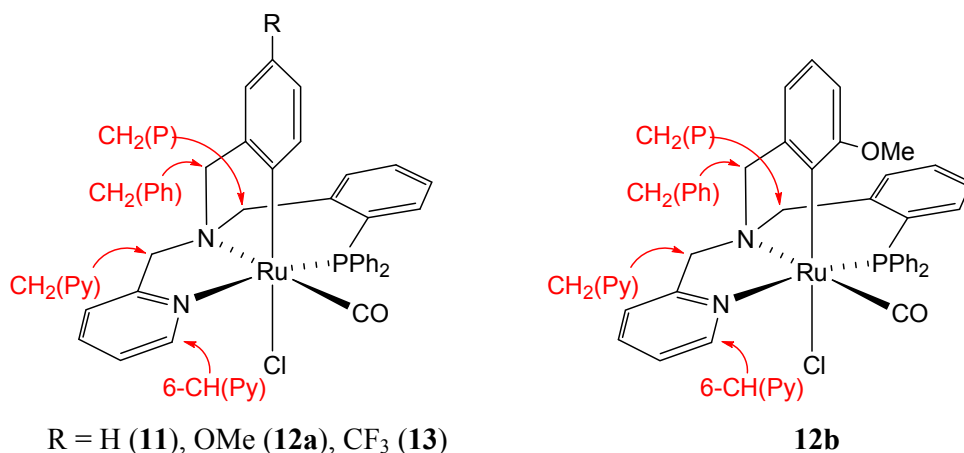
10a (98 %). ^1H NMR (300.13 MHz, CD_3OD , RT, ppm): $\delta = 8.25$ -6.26 (37H, H(Ar)), 4.40 (brd, $J = 14.2$ Hz, 1H, $\text{CH}_2(\text{Py})$), 4.18 (pt, $J = 12.5$ Hz, 2H, $\text{CH}_2(\text{Py})$, $\text{CH}_2(\text{Ph})$), 3.91 (br, 1H, $\text{CH}_2(\text{P})$), 3.82 (d, $J = 14.7$ Hz, 1H, $\text{CH}_2(\text{Ph})$), 3.61 (br, 1H, $\text{CH}_2(\text{P})$), and -13.46 (pt, $J = 22.3$ Hz, RuH). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.48 MHz, CD_3OD , RT, ppm): $\delta = 204.94$ (pt, $J = 15.0$ Hz, CO), 157.59 (brs, 2-C(Py)), 154.07 (brs, 6-CH(Py)), 138.12-123.88 (45C, Ar), 123.97 (q, $J = 273.4$ Hz, CF_3), 64.53 (brs, 2C, $\text{CH}_2(\text{Py})$, $\text{CH}_2(\text{P})$), and 61.64 (br, $\text{CH}_2(\text{Ph})$). $^{19}\text{F}\{^1\text{H}\}$ NMR (282.33 MHz, CD_3OD , RT, ppm): $\delta = -62.66$ (s). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.42 MHz, CD_3OD , 298 K, ppm): $\delta = 41.85$ (AB system, $J = 255.7$ Hz, PPh_3) and 40.52 (AB system, $J = 255.7$ Hz, PPh_2).

10a (73 %). ^1H NMR (500.13 MHz, CD_3OD , 213 K, ppm): $\delta = -13.22$ (pt, $J = 22.6$ Hz, RuH). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.46 MHz, CD_3OD , 213, ppm): $\delta = 41.64$ (AB system, $J = 254.3$ Hz, PPh_3) and 40.75 (AB system, $J = 254.3$ Hz, PPh_2).

10a' (25 %). ^1H NMR (500.13 MHz, CD_3OD , 213 K, ppm): $\delta = -12.87$ (dd, $J = 26.8$, 14.6 Hz, RuH). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.46 MHz, CD_3OD , 213, ppm): $\delta = 43.98$ (AB system, $J = 253.3$ Hz, PPh_3) and 40.17 (AB system, $J = 253.3$ Hz, PPh_2).

10c (2 %). ^1H NMR (300.13 MHz, CD_3OD , RT, ppm): $\delta = -11.33$ (pt, $J = 21.6$ Hz, RuH). $^{19}\text{F}\{^1\text{H}\}$ NMR (282.33 MHz, CD_3OD , RT, ppm): $\delta = -62.76$ (s). ^1H NMR (500.13 MHz, CD_3OD , 213 K, ppm): $\delta = -11.05$ (dd, $J = 24.1$, 17.3 Hz, RuH). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.46 MHz, CD_3OD , 213, ppm): $\delta = 43.41$ (d, $J = 256.3$ Hz, PPh_3) and 36.90 (d, $J = 256.3$ Hz, PPh_2).

Preparation and characterization of the complexes $[\text{RuCl}(\text{CO})(\kappa^4\text{N},\text{N}',\text{C},\text{P}-\text{L})]$ ($\text{L} = \text{L1}$ (11**), L2 (**12**), L3 (**13**)).** Suspensions of a mixture of isomers of the complexes $[\text{RuH}(\text{CO})(\text{PPh}_3)(\kappa^3\text{N},\text{N}',\text{P}-\text{LH})]\text{Cl}$ (500.0 mg, 0.555 mmol of **8**, 0.537 mmol of **9** or 0.516 mmol of **10**) in 20 mL of 2-ethoxyethanol were stirred for 2 days under reflux. Then, the resulting solution was vacuum-dried and the residue was recrystallized from CH_2Cl_2 /pentane, washed with Et_2O and vacuum-dried to give an analytical pure compound. Yield: **11**, 290.7 mg (82 %); **12**, 257.1 mg (72 %); **13**, 293.9 mg (81 %). Crystals of **11-13**, suitable for X-ray analysis were obtained by crystallization from CH_2Cl_2 /pentane solutions.



Compound **11**. Anal. calcd for $C_{33}H_{28}ClN_2OPRu$: C, 62.31; H, 4.44; N, 4.40. Found: C, 62.55; H, 4.64; N, 4.39. IR (cm^{-1}): $\nu(CO)$ 1920 (s). HRMS (μ -TOF): $C_{33}H_{28}ClN_2OPRu$ $[M-Cl]^+$: calc. 601.0986, found 601.1025. 1H NMR (500.13 MHz, CD_2Cl_2 , RT, ppm): δ = 8.7 (brptd, J = 5.5, 2.7 Hz, 1H, 6-CH(Py)), 7.7-6.3 (m, 21H, H(Ar)), 5.62 (d, J = 13.1 Hz, 1H, *pro-R*-CH₂(P)), 5.59 (d, J = 14.6 Hz, 1H, *pro-S*-CH₂(Py)), 4.58 (d, J = 16.9 Hz, 1H, *pro-R*-CH₂(Ph)), 4.09 (d, J = 14.3 Hz, 1H, *pro-R*-CH₂(Py)), 4.00 (dd, J = 13.0, 3.1 Hz, 1H, *pro-S*-CH₂(P)), and 3.80 (d, J = 16.9 Hz, 1H, *pro-S*-CH₂(Ph)). $^{13}C\{^1H\}$ NMR (125.77 MHz, CD_2Cl_2 , RT, ppm): δ = 205.14 (d, J = 18.2 Hz, CO), 167.39 (d, J = 12.6 Hz, CRu), 157.79 (s, 2-C(Py)), 151.59 (s, 6-CH(Py)), 146.16 (s, 2-C(Ph)), 142.18 (d, J = 18.9 Hz, 2-C(PhP)), 139.44 (s, CH(Ar)), 137.10 (s, CH(Ar)), 135.40 (s, CH(Ar)), 134.7 (d, J = 10.1 Hz, 2C, CH(Ar)), 133.57 (d, J = 8.8 Hz, CH(Ar)), 132.81 (d, J = 8.8 Hz, 2C, CH(Ar)), 131.92 (s, C(Ar)), 131.55 (s, C(Ar)), 131.26 (d, J = 1.3 Hz, CH(Ar)), 129.79 (d, J = 2.5 Hz, CH(Ar)), 129.26 (d, J = 36.5 Hz, C(Ar)), 128.32 (d, J = 5.8 Hz, CH(Ar)), 128.97 (d, J = 2.1 Hz, CH(Ar)), 127.62 (d, J = 10.1 Hz, 2C, CH(Ar)), 127.06 (d, J = 9.9 Hz, 2C, CH(Ar)), 126.05 (s, CH(Ar)), 123.96 (d, J = 2.5 Hz, CH(Ar)), 121.64 (d, J = 2.5 Hz, CH(Ar)), 120.46 (s, CH(Ar)), 118.55 (s, CH(Ar)), 71.14 (s, CH₂(Py)), 65.96 (s, CH₂(Ph)), and 64.86 (d, J = 6.4 Hz, CH₂(P)). $^{31}P\{^1H\}$ NMR (202.46 MHz, CD_2Cl_2 , RT, ppm): δ = 56.28 (s).

Compound **12a,b**. The isolated solid consists of a mixture of isomers in *ca.* 50/50 (**12a/12b**) molar ratio before crystallization. By crystallization a 64/36 (**12a/12b**) molar ratio was obtained. Anal. calcd. for $C_{34}H_{30}ClN_2O_2PRu$: C, 61.31; H, 4.54; N, 4.20. Found: C, 61.35; H, 4.66; N, 4.09. IR (cm^{-1}): $\nu(CO)$ 1936 (brs). HRMS (μ -TOF): $C_{34}H_{30}ClN_2O_2PRu$ $[M-Cl]^+$: calc. 631.1092, found 631.1120.

12a (64 %). 1H NMR (500.13 MHz, CD_2Cl_2 , RT, ppm): δ = 8.72 (ddd, J = 4.7, 1.6, 0.8 Hz, 1H, 6-CH(Py)), 7.80-6.57 (m, 16H, H(Ar)), 6.55 (pt, J = 7.8 Hz, 2H, H(Ar)), 6.22

(dd, $J = 9.1, 2.9$ Hz, 1H, H(Ar)), 6.07 (d, $J = 2.9$ Hz, 1H, H(Ar)), 4.62 (d, $J = 16.8$ Hz, 1H, *pro-S*-CH₂(Py)), 4.58 (d, $J = 17.0$ Hz, 1H, *pro-R*-CH₂(Ph)), 4.11 (dd, $J = 14.3, 4.4$ Hz, 1H, *pro-R*-CH₂(P)), 4.03 (ddd, $J = 13.0, 3.3$ Hz, 1H, *pro-S*-CH₂(P)), 3.86 (d, $J = 16.9$ Hz, 1H, *pro-R*-CH₂(Py)), 3.81 (d, $J = 17.6$ Hz, 1H, *pro-S*-CH₂(Ph)), and 3.26 (s, 3H, OMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.77 MHz, CD₂Cl₂, RT, ppm): $\delta = 205.22$ (d, $J = 18.2$ Hz, CO), 157.74 (s, 2-C(Py)), 155.56 (s, C(OMe)), 154.63 (d, $J = 11.3$ Hz, CRu), 151.62 (s, 6-CH(Py)), 146.39 (s, 2-C(Ph)), 142.02 (d, $J = 18.5$ Hz, 2-C(PhP)), 139.26 (s, CH(Ar)), 137.04 (s, CH(Ar)), 135.52 (s, CH(Ar)), 134.72 (d, $J = 10.3$ Hz, 2C, CH(Ar)), 133.57 (d, $J = 9.2$ Hz, 1C, CH(Ar)), 132.86 (d, $J = 9.7$ Hz, 2C, CH(Ar)), 131.22 (d, $J = 1.6$ Hz, CH(Ar)), 129.74 (d, $J = 1.9$ Hz, CH(Ar)), 128.94 (d, $J = 1.8$ Hz, CH(Ar)), 128.20 (dd, $J = 21.0, 5.2$ Hz, CH(Ar)), 129.31 (d, $J = 28.0$ Hz, C(Ar)), 127.61 (d, $J = 10.0$ Hz, 2C, CH(Ar)), 127.04 (d, $J = 10.0$ Hz, 2C, CH(Ar)), 124.89 (s, CH(Ar)), 123.85 (d, $J = 1.8$ Hz, CH(Ar)), 121.88 (d, $J = 3.7$ Hz, CH(Ar)), 121.61 (d, $J = 1.7$ Hz, CH(Ar)), 114.45 (s, CH(Ar)), 112.25 (s, CH(Ar)), 105.53 (s, CH(Ar)), 71.10 (brs, CH₂(Py)), 66.08 (s, CH₂(Ph)), 64.90 (d, $J = 6.3$ Hz, CH₂(PPh₃)), and 54.82 (s, OMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.46 MHz, CD₂Cl₂, RT, ppm): $\delta = 56.51$ (s).

12b (34 %). ^1H NMR (500.13 MHz, CD₂Cl₂, RT, ppm): $\delta = 8.72$ (ddd, $J = 4.7, 1.6, 0.8$ Hz, 1H, 6-CH(Py)), 7.80-6.57 (m, 16H, H(Ar)), 6.55 (pt, $J = 7.8$ Hz, 2H, H(Ar)), 6.22 (dd, $J = 9.1, 2.9$ Hz, 1H, H(Ar)), 6.07 (d, $J = 2.9$ Hz, 1H, H(Ar)), 4.62 (d, $J = 16.8$ Hz, 1H, *pro-S*-CH₂(Py)), 4.58 (d, $J = 17.1$ Hz, 1H, *pro-R*-CH₂(Ph)), 4.11 (dd, $J = 14.3, 4.4$ Hz, 1H, *pro-R*-CH₂(P)), 4.03 (ddd, $J = 13.0, 3.3$ Hz, 1H, *pro-S*-CH₂(P)), 3.88 (d, $J = 16.9$ Hz, 1H, *pro-R*-CH₂(Py)), 3.81 (d, $J = 17.6$ Hz, 1H, *pro-S*-CH₂(Ph)), and 3.26 (s, 3H, OMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.77 MHz, CD₂Cl₂, RT, ppm): 205.51 (d, $J = 18.5$ Hz, CO), 163.95 (s, C(OMe)), 157.85 (s, 2-C(Py)), 154.25 (d, $J = 11.1$ Hz, CRu), 152.30 (s, 6-CH(Py)), 147.55 (s, 2-C(Ph)), 142.20 (d, $J = 18.7$ Hz, 2-C(PhP)), 136.79 (s, CH(Ar)),

135.34 (s, CH(Ar)), 134.58 (d, $J = 10.2$ Hz, 2C, CH(Ar)), 133.37 (d, $J = 9.0$ Hz, 1C, CH(Ar)), 132.48 (d, $J = 9.9$ Hz, 2C, CH(Ar)), 131.05 (d, $J = 1.5$ Hz, CH(Ar)), 129.63 (d, $J = 1.8$ Hz, CH(Ar)), 128.61 (d, $J = 1.8$ Hz, CH(Ar)), 128.35 (m, CH(Ar)), 127.56 (d, $J = 10.1$ Hz, 2C, CH(Ar)), 126.86 (d, $J = 10.0$ Hz, 2C, CH(Ar)), 124.61 (s, CH(Ar)), 123.88 (d, $J = 1.5$ Hz, CH(Ar)), 123.79 (d, $J = 2.0$ Hz, CH(Ar)), 121.92 (d, $J = 3.7$ Hz, CH(Ar)), 121.43 (d, $J = 1.6$ Hz, CH(Ar)), 113.93 (s, CH(Ar)), 112.03 (s, CH(Ar)), 106.54 (s, CH(Ar)), 71.22 (bs, CH₂(Py)), 66.73 (s, CH₂(Ph)), 65.05 (d, $J = 6.2$ Hz, CH₂(PPh₃)), and 54.82 (s, OMe). $^3\text{P}\{^1\text{H}\}$ NMR (202.46 MHz, CD₂Cl₂, RT, ppm): $\delta = 55.71$ (s).

Compound **13**. Anal. calcd for C₃₄H₂₇ClF₃N₂OPRu: C, 58.00; H, 3.87; N, 3.98. Found: C, 58.30; H, 3.94; N, 3.92. IR (cm⁻¹): $\nu(\text{CO})$ 1922 (s). HRMS (μ -TOF): C₃₄H₂₇ClF₃N₂OPRu [M+H]⁺: calc. 705.0624, found 705.0634. ^1H NMR (500.13 MHz, CD₂Cl₂, RT, ppm): $\delta = 8.7$ (brptd, $J = 5.7, 2.7$ Hz, 1H, 6-CH(Py)), 7.7-6.3 (m, 20H, H(Ar)), 5.72 (d, $J = 12.9$ Hz, 1H, *pro-R*-CH₂(P)), 5.62 (d, $J = 14.4$ Hz, 1H, *pro-S*-CH₂(Py)), 4.67 (d, $J = 17.0$ Hz, 1H, *pro-R*-CH₂(Ph)), 4.17 (d, $J = 14.4$ Hz, 1H, *pro-R*-CH₂(Py)), 4.08 (dd, $J = 13.1, 3.1$ Hz, 1H, *pro-S*-CH₂(P)), and 3.90 (d, $J = 17.1$ Hz, 1H, *pro-S*-CH₂(Ph)). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.77 MHz, CD₂Cl₂, RT, ppm): $\delta = 204.62$ (d, $J = 18.0$ Hz, CO), 177.23 (d, $J = 10.7$ Hz, CRu), 157.43 (s, 2-C(Py)), 151.52 (s, 6-CH(Py)), 146.50 (s, 2-C(Ph)), 142.00 (d, $J = 17.6$ Hz, 2-C(PhP)), 139.30 (s, CH(Ar)), 137.42 (s, CH(Ar)), 135.63 (s, CH(Ar)), 134.73 (d, $J = 10.3$ Hz, 2C, CH(Ar)), 134.26 (s, C(Ar)), 133.61 (d, $J = 9.2$ Hz, CH(Ar)), 132.38 (d, $J = 9.6$ Hz, 2C, CH(Ar)), 131.56 (s, CH(Ar)), 131.24 (s, C(Ar)), 130.04 (d, $J = 2.5$ Hz, CH(Ar)), 129.12 (d, $J = 2.1$ Hz, CH(Ar)), 128.80 (s, C(Ar)), 128.54 (d, $J = 2.1$ Hz, CH(Ar)), 127.75 (d, $J = 10.1$ Hz, 2C, CH(Ar)), 127.19 (d, $J = 10.0$ Hz, 2C, CH(Ar)), 125.42 (q, $J = 171.5$ Hz, CF₃), 124.24 (d, $J = 1.70$ Hz, CH(Ar)), 122.60 (q, $J = 30.9$ Hz, C(CF₃)), 121.80 (s, CH(Ar)), 114.40

(q, $J = 3.6$ Hz, CH(Ar)), 71.25 (s, CH₂(Py)), 65.71 (s, CH₂(Ph)), and 64.87 (d, $J = 5.2$ Hz, CH₂(P)). $^{19}\text{F}\{^1\text{H}\}$ NMR (282.33 MHz, CD₂Cl₂, RT, ppm): $\delta = -61.85$ (s). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.46 MHz, CD₂Cl₂, RT, ppm): $\delta = 55.12$ (s).

Crystal structure determination of complexes 1, 2, 5c, 10a, 11a, 12a,b and 13a. X-ray diffraction data were collected at 100(2) K (complexes 1, 2, 5c, 10a, 12a,b and 13a) or 120(2) K (complex 11a) using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) using a narrow frame algorithm ($\Delta\omega = 0.3^\circ$) on a Smart APEX Bruker diffractometer. Intensities were integrated and corrected for absorption effects with SAINT¹³ and SADABS¹⁴ programs, integrated in APEX2 package. The structures were solved by direct methods with SHELXS-2013 or SHELXS-2017¹⁵ and refined by full-matrix least-squares refinements in F^2 with SHELXL-2014 or SHELXL-2017¹⁶ programs included in WingX package.¹⁷ Most of the hydrogen atoms have been included in the model in calculated positions and refined with a riding model. Special details about the presence of solvent or disorder are listed below.

Crystal Data for 1: C₄₂H₄₃F₁₂N₂PRuSb₂·2(CH₂Cl₂); $M = 1349.17$; yellow prism, $0.220 \times 0.250 \times 0.300$ mm; triclinic $P\bar{1}$; $a = 12.2908(5)$, $b = 13.7900(6)$, $c = 15.7626(7)$ Å; $\alpha = 97.0026(5)^\circ$, $\beta = 102.2943(5)^\circ$, $\gamma = 104.4687(5)^\circ$; $V = 2483.87(18)$ Å³; $Z = 2$; $\rho_{\text{calcd}} = 1.804$ g cm⁻³; $\mu = 1.707$ cm⁻¹; min. and max. transmission factors 0.5963 and 0.7257; $2\theta_{\text{max}} = 57.306^\circ$; 30558 reflections collected; 11592 unique reflections ($R_{\text{int}} = 0.0206$); number of data/restraints/parameters: 11592/0/603; final $GOF = 1.022$; $R_I = 0.0249$ [10410 reflections, $I > 2\sigma(I)$], $wR2 = 0.0624$ for all data; largest difference peak: 0.894 e Å⁻³. A chlorine atom of the solvent has been found to be disordered. It has been included in the model in two positions with complementary occupancy factors (0.858/0.142(5)). The minor component has been isotropically refined.

Crystal Data for 5c: C₃₉H₄₀F₁₂N₅OPRuSb₂·3/2(CH₂Cl₂); *M* = 1325.69; colorless prism, 0.130 × 0.150 × 0.200 mm; triclinic *P* $\bar{1}$; *a* = 12.1760(6), *b* = 12.8773(6), *c* = 16.3228(8) Å; α = 81.4250(10)°, β = 85.5510(10)°, γ = 71.8340(10)°; *V* = 2403.3(2) Å³; *Z* = 2; ρ_{calcd} = 1.832 g cm⁻³; μ = 1.711 cm⁻¹; min. and max. transmission factors 0.7302 and 0.8227; $2\theta_{\text{max}}$ = 57.312°; 28309 reflections collected; 11215 unique reflections (*R*_{int} = 0.0302); number of data/restraints/parameters: 11215/3/601; final *GOF* = 1.033; *R*_I = 0.0414 [9271 reflections, *I* > 2σ(*I*)], *wR*₂ = 0.1003 for all data; largest difference peak: 2.336 e Å⁻³. The asymmetric unit contains a ruthenium complex, two SbF₆ counterions and dichloromethane solvent. The counterions have been found to be in three sites, with 1, 0.5 and 0.5 occupancy factors. The second site lies on a special position, while the third one is found to share the volume with a disordered dichloromethane (with 0.5 occupancy factor). Geometrical restraints concerning C–Cl and Sb–F bond lengths have been used in the refinement. At the end of the refinement, when convergence is achieved, highest residual density peaks are observed close to disordered Sb. They have no chemical sense.

Crystal Data for 10a: C₅₂H₄₄ClF₃N₂OP₂Ru·3(C₂H₆O); *M* = 1106.55; colorless prism, 0.100 × 0.115 × 0.130 mm; triclinic *P* $\bar{1}$; *a* = 13.1863(11), *b* = 14.5593(12), *c* = 15.1056(13) Å; α = 99.1230(10)°, β = 104.1100(10)°, γ = 103.1760(10)°; *V* = 2667.2(4) Å³; *Z* = 2; ρ_{calcd} = 1.378 g cm⁻³; μ = 0.462 cm⁻¹; min. and max. transmission factors 0.8062 and 0.9705; $2\theta_{\text{max}}$ = 56.664°; 31264 reflections collected; 12697 unique reflections (*R*_{int} = 0.0463); number of data/restraints/parameters: 12697/2/664; final *GOF* = 1.060; *R*_I = 0.0561 [10206 reflections, *I* > 2σ(*I*)], *wR*₂ = 0.1297 for all data; largest difference peak: 1.241 e Å⁻³. Two of the three independent solvent molecules have been found to be disordered. Their disordered fragments (methyl or hydroxyl group) have been included in the model in two sets of positions and isotropically

refined. Hydrido ligand and hydrogen atoms of OH groups of solvent molecules involved in hydrogen bonds have been included in the model in observed positions and freely refined.

Crystal Data for 11a: C₃₃H₂₈ClN₂OPRu·CH₂Cl₂; *M* = 720.99; yellow plate, 0.075 × 0.175 × 0.200 mm; monoclinic *P*2₁/*c*; *a* = 16.6067(8), *b* = 9.8577(5), *c* = 19.3399(9) Å; *β* = 102.7540(10)°; *V* = 3087.9(4) Å³; *T* = 120(2) K; *Z* = 4; *ρ*_{calcd} = 1.551 g cm⁻³; *μ* = 0.850 cm⁻¹; min. and max. transmission factors 0.7982 and 0.9044; 2*θ*_{max} = 54.864°; 42123 reflections collected; 7022 unique reflections (*R*_{int} = 0.0416); number of data/restraints/parameters: 7022/0/378; final *GOF* = 1.051; *R*_I = 0.0418 [6016 reflections, *I* > 2σ(*I*)], *wR*2 = 0.1166 for all data; largest difference peak: 0.923 e Å⁻³. A carbon and a chlorine atom of dichloromethane solvent have been found to be disordered. They have been included in the model in two sets of positions and isotropically refined with complementary occupancy factors (0.585/0.415(8)).

Crystal Data for 12a,b: C₃₄H₃₀ClN₂O₂PRu·H₂O; *M* = 684.10; yellow plate, 0.080 × 0.150 × 0.230 mm; monoclinic *C*2/*c*; *a* = 19.1243(17), *b* = 11.2815(10), *c* = 28.078(3) Å; *β* = 101.4340(10)°; *V* = 5937.7(9) Å³; *T* = 100(2) K; *Z* = 8; *ρ*_{calcd} = 1.531 g cm⁻³; *μ* = 0.711 cm⁻¹; min. and max. transmission factors 0.6830 and 0.7457; 2*θ*_{max} = 56.608°; 33705 reflections collected; 7225 unique reflections (*R*_{int} = 0.0779); number of data/restraints/parameters: 7225/0/372; final *GOF* = 1.041; *R*_I = 0.0584 [4935 reflections, *I* > 2σ(*I*)], *wR*2 = 0.1470 for all data; largest difference peak: 0.916 e Å⁻³.

Part of a phenyl group, the methoxo fragment and solvent water have been found to be disordered. They have been included in the model in two sets of positions and refined with complementary occupancy factors. A common value has been used to isotropically refine minor and major components of carbon and oxygen atoms.

Crystal Data for 13a: C₃₄H₂₇ClF₃N₂OPRu·CH₂Cl₂; $M = 788.99$; yellow prism, $0.100 \times 0.110 \times 0.150$ mm; monoclinic $P2_1/n$; $a = 12.6163(8)$, $b = 10.4172(6)$, $c = 24.8162(15)$ Å; $\beta = 93.6150(10)^\circ$; $V = 3255.0(3)$ Å³; $Z = 4$; $\rho_{\text{calcd}} = 1.610$ g cm⁻³; $\mu = 0.827$ cm⁻¹; min. and max. transmission factors 0.8421 and 0.9281; $2\theta_{\text{max}} = 56.634^\circ$; 41602 reflections collected; 7975 unique reflections ($R_{\text{int}} = 0.0519$); number of data/restraints/parameters: 7975/0/414; final $GOF = 1.060$; $R_I = 0.0675$ [6547 reflections, $I > 2\sigma(I)$], $wR2 = 0.1742$ for all data; largest difference peak: 1.779 e Å⁻³. One of the chlorine atoms of dichloromethane solvent has been found to be disordered and isotropically refined with complementary occupancy factors (0.754/0.246(5)) in two positions.

ASSOCIATED CONTENT

Supporting Information Available: Kinetic studies for the isomerization of complex **10**. Selected NMR spectra of compounds **11-13**. Crystal structure determination of complex **2**. Intermolecular interactions details of complex **5c**. Ring puckering parameters for complexes **1, 2, 5c, 10a, 11a, 12a,b** and **13a**. CCDC 1829050-1829056 contains the supplementary crystallographic data for this paper (**1, 2, 5c, 10a, 11a, 12a,b, 13a** complexes in CIF format). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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